



Tribocorrosion properties of metallic materials and effects of metal release

Jellesen, Morten Stendahl; Hilbert, Lisbeth Rischel; Møller, Per

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Tribocorrosion properties of metallic materials and effects of metal release

Ph. D. Thesis

August 2007

by

Morten Stendahl Jellesen


Department of Manufacturing Engineering and Management
Technical University of Denmark (DTU)
DK - 2800 Kgs. Lyngby.

Preface

The present thesis is submitted in candidacy for a Ph. D. - degree from the Technical University of Denmark (DTU). The work presented was carried out under supervision of Professor Per Møller and Associate Professor Lisbeth Rischel Hilbert during the period May 2004 to May 2007 at the Department of Manufacturing Engineering and Management.

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Kgs. Lyngby 14/8/2007



Morten Stendahl Jellesen

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Abstract

This work investigates degradation of metallic materials used in critical contact situations, where metal release can cause metal contamination of food or allergic reactions to skin or tissue. When designing and selecting materials for food processing equipment it is important to consider the material properties with respect to the entire system surrounding it. Thus it is important to have methods available for investigating material behaviour in complex systems as food products, and additionally with respect to the mechanical impacts that might take place during processing. The construction and modification of tribometer setups has made it possible to study the electrochemical degradation during simulated, but well controlled, tribocorrosion conditions.

The main results of this work are included in form of papers given in appendices. Appendix I reviews a broad range of published literature on metal release in the food industry. Appendices II and III focuses on a block-on-ring test setup, used for investigating equipment in the food industry, where sliding wear occurs. Appendices IV and V investigate various surface modifications of stainless steel, when exposed to erosion-corrosion and the papers given in appendices VI to VIII illustrate the principles of tribocorrosion and consequent metal release under exposure to mild wear.

The test results combined with Pourbaix diagrams, validating the thermodynamics of possible material degradation mechanisms, have resulted in new materials solutions suggested for food processing equipment. Investigations of various surface modifications of stainless steel have given reliable and useful data for developing wear and corrosion resistant stainless steel surfaces. Especially the use of diamond-like carbon coatings together with low temperature gaseous nitriding seems promising in this respect, since both wear and corrosion properties are significantly improved as compared to untreated stainless steel. The health effects of metal release from food processing equipment are estimated to be negligible, since metals being toxic at low levels are avoided in processing equipment. Possible release of metals as nickel, iron, chromium, molybdenum, tungsten or cobalt is likely to be diluted to a large extent in the large tonnages of food products. Nevertheless, uncontrolled metal contributions to food are not advisable and the lifetime of equipment can be prolonged if improved materials are implemented instead of continuously replacing parts that have degraded due to corrosion and wear.

Resume

Denne afhandling beskriver nedbrydning af metalliske materialer benyttet i kritiske applikationer, hvor metal afsmitning kan resultere i metal forurening af fødevarer eller skabe allergiske reaktioner på hud eller væv. Ved design og udvælgelse af materialer til fødevare procesudstyr skal materialeegenskaber karakteriseres med henblik på hele det omkringliggende system til udstyret. Derfor er det vigtigt at have metoder til rådighed, der kan undersøge materialers opførsel med hensyntagen til komplekse systemer, såsom fødevare produkter og eventuelle mekaniske påvirkninger, som kan finde sted ved processering. Opbygning og modificering af tribometer opstillinger har gjort det muligt at studere den elektrokemiske nedbrydning under simulerede, men vel kontrollerede tribokorrosions-betingelser.

Hovedresultaterne er inkluderet i form af artikler givet i appendiks. Appendiks I opsummerer en bred vifte af publiceret litteratur om metal afgivelse i fødevareindustrien. Appendiks II og III fokuserer på et blok-on-ring test setup, som bruges til at undersøge slid og korrosionsegenskaber af udstyr, hvor glidende slid foregår. Appendiks IV og V undersøger en række overflademodifikationer af rustfrit stål under påvirkning af erosionskorrosion og artiklerne i appendiks VI til VIII illustrerer principperne i tribokorrosion og undersøger metal afsmitning under eksponering for mildt slid.

Testresultaterne sammenlignes med Pourbaix diagrammer, der viser termodynamikken for mulige materiale nedbrydningsmekanismer. Resultatet heraf er at nye materialer er blevet foreslået til brug i fødevare procesudstyr. Undersøgelser af en række overflademodifikationer har givet reproducerbare og brugbare data til udvikling af slid- og korrosionsbestandige rustfri stål overflader. Specielt brugen af diamant lignende karbon belægninger kombineret med lavtemperatur gasnitring virker lovende i denne henseende, siden både slid såvel som korrosionsegenskaber er tydeligt forbedret sammenlignet med ubehandlet rustfrit stål. Helbredseffekterne af metalafsmitning fra fødevare proces udstyr er estimeret til at være minimale, da metaller, giftige i små mængder helt undgås i procesudstyr til fødevareproduktion. Eventuel afsmitning af metaller som nikkel, jern, krom, molybdæn, wolfram eller kobolt bliver ofte fortyndet i de store mængder fødevarer, der bliver processeret. Ikke desto mindre er ukontrollerbar metalafsmitning uønskelig og udstyrets levetid kan forlænges, hvis forbedrede materialer implementeres i stedet for kontinuerlig udskiftning af udstyrsdele, der er nedbrudt ved korrosion eller slid.

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Appended papers

- I A review of metal release in the food industry.
- II A block-on-ring tribocorrosion setup for combined electrochemical and friction testing.
- III Corrosion and wear properties of materials used for minced meat production.
- IV Erosion-corrosion behavior of innovative hardening treatments and coatings on stainless steels for food industry applications.
- V Erosion-corrosion and corrosion properties of DLC coated gas-nitrided austenitic stainless steel
- VI Nickel-containing coins: a health risk for nickel-sensitive individuals?
- VII Investigation into nickel release rates from coins.
- VIII The electrochemical deposition of tin-nickel alloys and the corrosion properties of the coating.

List of publications

1.
M.S. Jellesen, A. Rasmussen and L.R. Hilbert
A review of metal release in the food industry.
Materials and Corrosion, 2006, **57**, 5,1-10.
(Included as Appendix I)
2.
M. S. Jellesen, M. Ø. Hansen, L. R. Hilbert, P. Møller
A block-on-ring tribocorrosion setup for combined electrochemical and friction testing.
Tribotest, 2007, **13**, 115-127.
(Included as Appendix II)
3.
M. S. Jellesen, M. Ø. Hansen, L. R. Hilbert, P. Møller
Corrosion and wear properties of materials used for minced meat production.
submitted July 2007 for publication in *Journal of Food Process Engineering*.
(Included as Appendix III)
4.
M. S. Jellesen, M. K. Hansen, L. R. Hilbert , P. Møller
Erosion-Corrosion Behavior of Innovative Hardening Treatments and Coatings on Stainless Steels for Food Industry Applications.
Journal of applied surface finishing, 2007, **2**, 1, 56-62.
(Included as Appendix IV)
5.
M. S. Jellesen, T. Christiansen, L. R. Hilbert , P. Møller
Erosion-corrosion and corrosion properties of DLC coated gas-nitrided austenitic stainless steel.
Submitted August 2007 for publication in *Wear*.
(Included as Appendix V)
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M.S. Jellesen, L.R. Hilbert, T. Menné, P. Møller
Nickel-containing coins: a health risk for nickel-sensitive individuals?
British Journal of Dermatology, 2006, **155**, 1301-1303.
(Included as Appendix VI)
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Plating and Surface Finishing, 2005, **92**, 36-41.
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M.S. Jellesen
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A conference paper in Danish, presented at DMS Vintermøde and in DMS proceedings: Korrosion - mekanismer, havarier og beskyttelse,
ISBN: 87-87535-35-1, pp. 187-204, 2006.
11.
M. S. Jellesen, M. Ø. Hansen, L. R. Hilbert, P. Møller
Setup for combined electrochemical and friction testing during sliding wear.
A conference paper presented at Nordtrib 2006, Copenhagen. In The 12th Nordic Symposium on Tribology, DTU Tryk, ISBN:87-904 16-17-1, 2006.
12.
M. S. Jellesen, L. R. Hilbert, P. Møller
Erosion-corrosion behaviour of innovative hardening treatments and coatings on stainless steels for food industry applications.
A conference paper presented at Sur/Fin and in AESF proceedings Sur/Fin, Milwaukee, USA, 2006.
13.
M. S. Jellesen, L. R. Hilbert, P. Møller
Erosion-corrosion behaviour of innovative hardening treatments.
A conference paper presented at Eurocorr, Maastricht and in Eurocorr Proceedings, 2006.
14.
M. S. Jellesen, L. R. Hilbert T. Menné, P. Møller
Studies on tribocorrosion explain low nickel release.
A conference paper in Eurocorr Proceedings, 2006.
15.
M. S. Jellesen, L. R. Hilbert, P. Møller
Corrosion and Wear in the Food Industry.
A conference paper presented at Nordic Corrosion Congress, NKM 14, Copenhagen, 2007.

1. Introduction

This work investigates degradation of metallic materials used in critical contact situations, where metal release can cause contamination of food, or allergic reactions to skin or tissue. Especially for processing equipment in the food industry this is an under explored research area. The metal content of raw and final food products are often well monitored by authorities, but only a small amount of work has been reported concerning monitoring of metal release during processing. This work is a part of the MetalinFood project (2003-2007), which has aimed at identifying process steps with possible metal release and to suggest improved material solutions and design for enhanced lifetime of process equipment. The focus of this work was to simulate material degradation in the laboratory and to study details of important degradation mechanisms and material properties.

Degradation by corrosion is of most concern in the food industry. Knowing the food products pH, salt content, viscosity and temperature it is most often possible to select appropriate materials given the wide range of stainless steel types offered on the market. This work presents corrosion investigations of materials used in fruit and vegetable juice production and compare these laboratory results with metal release monitored at a juice production site.

Wear is also a concern in the food industry, but most often processing equipment is designed to avoid severe wear. In some cases food products are processed to great extent and wear is almost unavoidable. If process equipment is degraded faster than expected from separate evaluations of corrosion and wear properties, tribocorrosion may be a dominant material degradation mechanism. The construction and modification of tribometer setups has made it possible to study the electrochemical degradation during simulated, but well controlled tribocorrosion conditions. Three different tribocorrosion conditions have been investigated in this work. A method for testing surfaces exposed to erosion-corrosion has been developed and metal degradation by sliding wear in aggressive food products has been investigated using a block on ring setup. Such tribocorrosion setups allow for determination of metal release in cases where processing equipment is exposed to erosive-corrosive conditions or sliding wear contact. Finally a setup was build to simulate hand rubbing of nickel coatings, stainless steel and nickel-containing coins, illustrating the principles of tribocorrosion under mild wear conditions. Pourbaix diagrams have been constructed and are used to validate the thermodynamics of possible material degradation mechanisms.

A review of literature concerning metal release into food products and possible health risks of individual metals are presented in chapter 2. A short introduction to wear, corrosion and tribocorrosion is given in chapter 3 together with a description of setups and techniques used to investigate such material properties. Chapter 4 gives a short introduction to materials and surface modifications used in the food industry. Methods developed and used in this work are shortly described in chapter 5. As the main part of results obtained already has been published (in appended papers I to VIII) only background information for these results are presented and discussed in chapter 6. Appended papers are shortly summarized in chapter 7 before discussion, conclusion and outlook are presented in chapters 8 to 10.

2. Metal release in the food industry

Recent trends in global food production, processing, distribution, and preparation are creating an increasing demand for food safety research in order to ensure a safe food supply. The EU integrated approach to food safety aims at assuring a high level of food safety through coherent farm-to-table measures and adequate monitoring, while ensuring the effective functioning of the internal market.¹ Metals and alloys are used as food contact materials in industrial processing equipment, from harvest until the product reaches the consumer and thus metal contamination of food products can occur at any point in the production chain. Stainless steel is the most used processing equipment material in the food industry. Corrosion can nevertheless become a problem when stainless steel is exposed to aggressive food products (table 2.1), or chlorine containing products used for sanitizing or wear.

Table 2.1 pH of common food products.²

Fruits		Vegetables	
Apples	3.0–3.5	Potatoes	5.5–6.0
Oranges	3.0–4.0	Cabbage	5.0–5.5
Lemons	2.0–2.5	Carrots	5.0–5.5
Tomatoes	4.0–4.5	Beet	5.0–5.5
Raspberries	3.0–3.5	Pickles	3.0–3.5
Dairy Products		Beverages	
Cow's Milk	6.0–6.5	Beers	4.0–5.0
Butter	6.0–6.5	Fruit drinks	2.0–4.0
Cheeses	5.0–6.5	Wines	3.0–4.0
Meat and Fish		Bakery	
Fish	6.0	Bread	5.0–6.0
Meats	7.0	Wheat Flour	5.5–6.5

Not just financial inconvenience, related to renewing damaged equipment, but also continuous metal release in the form of ions or small wear particles is undesired, since such metal release can cause allergy, be toxic (Hg, Pb, Cd and As should always be avoided in materials used for food contact) or cause other health related problems, if released in large amounts.

Food products have their own natural content of metals and therefore nickel allergy sensitized individuals can be advised to avoid certain food products.³ If there, additionally to the natural metal content, is a metal release from metallic surfaces in direct contact with the food product, undesirable effects may occur to sensitized individuals.⁴ Besides possible dermatitis aggravation for severe nickel allergists, there is also hygienic aspects linked to degradation of process equipment in the food industry caused by corrosion and wear. Surface topography changes as a

consequence of corrosion and/or wear is likely to cause increased microbial adhesion resulting in lower cleanability. Pitting potentials and critical pitting temperatures of as-extruded or electropolished austenitic stainless steel pipes have been investigated, showing that electropolishing makes an improvement in pitting resistance, but with a few scattered exceptions. The electropolishing minimizes pit initiation sites and it is thus expected that the cleanability of the electropolished surface is better.⁵ Microbial adhesion and the influence of surface roughness have also been investigated on welding areas of stainless steel, showing that for corroded surfaces (heat-affected and welded zones) bacterial counts were highest.⁶ Another study showed that the surface roughness of stainless steel had a minor effect on microbial parameters; however the corrosion resistance was improved by smoothing of the surface.⁷

2.1 Reported contamination of food by metals

For reviewing literature of metal release into food products the book *Metal Contamination of Food* by Conor Reilly⁸ is a good place to start. Much literature has been published on metal release from cans for food storing describing stress corrosion cracking in plain tinsplate food cans, product discoloration, filiform corrosion, pitting corrosion and loss of adhesion in enamelled food cans.^{9,10,11} The individual food handling and preparation by consumers is also described in literature, e.g. the release of nickel and other trace elements from electric kettles and coffee machines sold in the Danish market.^{12,13} Many of the kettles included in the investigations released more than 50 µg/l nickel to water. These results lead to a change of construction and design of electric kettles to ensure a nickel release lower than 50 µg/l nickel, which meant that a few kettles were withdrawn from the market. Nickel and chromium release from stainless steel cooking utilities have also been studied and apart from aberrant values associated with new pans on first use, the release of metals to the diet was found negligible.^{14,15} The amount of nickel derived from the utensils in standard portions of various “aggressive” foodstuffs tested was found to be 0-8 µg/portion. Investigations of nickel release from boiling water in stainless steel saucepans showed that nickel release could be correlated to the increasing acidity of the boiling water.¹⁶ The investigators advise patients with nickel allergy to avoid stainless steel cooking utensils, since lingonberries, rhubarb and apples may provide an acidic environment during processing and thus increase nickel release rates.

One obvious reason for metal contamination as a consequence of production is the presence of fragments of harvesting or processing equipment accidentally finding

their way into the food. Foods are routinely screened for such unwanted materials by one or a combination of standard cleaning operations carried out as a first step at food processing plants. Physical separation techniques as separation, filtration or washing can be used and screens are employed for sifting out larger particles and various types of metal detectors are used to pick up fragments that escape the sifting. Also tube or grid magnets can be used in processing of dry free flowing food products to remove small contaminating metallic (and magnetic) particles. The principle in magnetic separation and various metal detectors and x-ray examination systems has been thoroughly described elsewhere.¹⁷

This work focuses on the continuous metal release during processing, caused by corrosion and/or wear resulting in metal being released as ions or small particles (micro/nano size) which cannot be detected by commonly used methods. Only a few reports of metal release during production can be found in literature.^{18,19} Continuous metal release occurs most often as the result of misuse of equipment or by use of unsuitable metals. Cadmium, for instance, should not be used in parts for direct contact with food, but cadmium plated vessels have been used improperly and poisonings have resulted.²⁰ Also use of inappropriate materials for repair of equipment does occur at times. The replacement of corroded stainless steel pipe in a freezer unit by a copper tube taken from a discarded piece of equipment resulted in copper-contaminated products and several poisoning reports.⁸

Modern food processing is designed with full regard to hygiene and cleanliness, taking the type of food being processed into account, and with awareness of their compatibility with materials being used (often high quality stainless steel approved for food contact) there is little danger of metal release into the food product being processed.⁸ A document is available for manufactures, users and regulatory personnel with basic information and guidelines for passivation of stainless steel equipment in order to assure the successful corrosion resistant performance of stainless steel used for product contact surfaces.²¹ The purpose of the passivation process is to enhance the chromium fraction in the passive film²² and the main mechanism for this process is selective dissolution of predominantly iron.²³ The complete passivation process consists of mechanical cleaning, degreasing, inspection, the actual passivation (immersion or spraying of an oxidising acid), and rinsing.

2.2 Possible health risks from individual metals

The metal content of food products will depend on many factors, ranging from environmental conditions for the raw product to methods of production and processing into the final food product. Even in the same class of food, considerable variations in concentrations of metals can be found.⁸ Therefore the mean concentration of metals in food products does not necessarily give the exact amount of metal consumed by individuals even though the diet is known with great certainty. Nevertheless, knowledge of average and extreme levels of metals in foods is important when assessing public health consequences of food contamination.⁸

Metals being poisonous at low levels such as lead, cadmium and mercury should always be avoided in materials used for food contact. Lead poisoning can be acute or accumulate in the body and cause more chronic poisoning causing weakness, fatigue and intense abdominal pain. Mercury can also accumulate in the body and compounds of mercury are known to be more toxic than the metal itself.²⁴ Fish consumption is the major contributor to mercury in the diet and has caused strict controls on levels of mercury in fish of 0,5 mg/kg. Cadmium is normally found in most food products at low levels, unless contamination has occurred. Ingestion of cadmium at about 15 mg/kg can cause nausea, vomiting, abdominal cramps, headaches, diarrhoea or shock.

Apart from such metals being poisonous at low levels, many alloys used for processing equipment contain Ni, Fe, Cr, Mo, W or Co. It has been augmented that chromium, iron and nickel release from utensils contributes to nutrition in the diet.^{25,26} Still, such uncontrolled metal contributions are not advisable, since it can be difficult to distinguish between the amount of metal being toxic or essential for human metabolism and body function. Levels of the above mentioned metals in food products and their possible health risks are summarized in the following.

Ni:

Aggravation of dermatitis among nickel-sensitive women has been reported as well as aggravation of dermatitis after ingestion of chromate and cobalt. Recognition of hand eczema improvement after low-nickel dieting is also reported.²⁷ It has been estimated that the prevalence of nickel allergy in the Danish population is about 10% for women and 3% for men,^{28,29} among those 10% percent are sensitive to nickel in food.^{12,30} An investigation of food samples, representing the general population's diet, concludes that the dietary intake of nickel does not represent any health risk to the

general population, but that the risk of additional nickel exposure from metallic surfaces in direct contact with food may cause adverse effects to occur to sensitized individuals.³¹ An investigation of nickel in drinking water has shown development of eczema exacerbations in almost half of the nickel allergic patients, who had ingested an increased, yet not unrealistic (12 µg/kg body wt.), amount of nickel in water.³² A dose-response study has demonstrated that oral nickel exposure elicits skin reactions in nickel sensitive individuals,³³ but still nickel in food cannot always be considered as a source of health risks. Investigations even suggest that oral intake of small amounts of nickel apparently can prevent the development of nickel allergy.³⁴ According to the Council of Europe nickel intake via food does not cause hazards for the majority of consumers, however the council acknowledges investigations showing a flare-up of eczema through ingestion of even small amounts of orally ingested nickel.³⁵

Food is the major source of nickel exposure for the general population with an average intake about 170 µg per day. Food products naturally high in nickel include chocolate, soybeans, nuts, and oatmeal. The daily intake of nickel from drinking water is only 5-25 µg per day.³⁶ Consuming levels of nickel much greater than the levels normally found in food and water has been reported to produce lung disease in dogs and rats and to affect the stomach, blood, liver, kidneys, and immune system in rats and mice, as well as their reproduction and development.³⁷ It has been estimated that 1 % of the most nickel sensitized individuals may react with a systemic contact eczema at exposures to 0,22 - 0,35 mg nickel in addition to their normal diet. Exposure to 0,55 – 1,33 mg nickel will cause a systemic reaction in 10 % of the most sensitized individuals.³⁸ Eczema usually develops on skin that is directly exposed to Ni-containing objects. There are, however, people who develop eczema or blisters on non-exposed skin and it has been suggested that intake of Ni via food can have an enhancing effect for this group of people.³⁹

Fe:

Iron is present in all foods and beverages, as it is in all biological materials. In the human body iron is needed for the synthesis of blood pigments, as well as for many other essential activities of cells.⁸ Health risks due to iron deficiency are more reported than health risk due to increased iron intake, but in high doses all minerals are toxic and also iron toxicity can occur even though seldom reported. Consumption of iron tablets by children, who mistake them for sweets, has been one of the most frequent causes of iron poisoning. Treatment is iron-chelating compounds, binding

iron in the gut thus reducing further absorption and also detoxifying iron in plasma and tissues.⁴⁰ Ellenham et al. found that a dose of 180-300 mg/kg body weight may be lethal, whereas oral doses below 10-20 mg/kg body weight do not seem to induce systemic toxicity.⁴¹ Merrill et al. showed that an acute oral dose of 60 mg Fe/kg body weight can be lethal; characteristically poisoned subjects initially show nausea, vomiting and lethargy or coma, then an asymptomatic period for up to 24 hours, which is followed by gastrointestinal perforation, coma, convulsions, cardiovascular collapse and hepatic and renal failure.⁴² Iron release into food product has mainly been reported from canning of e.g. fruits, vegetables, meat and fish⁴³ and iron content up to 5800 mg/kg were found in a can of anchovies in sauce stored for four years.⁴⁴

Cr:

Trivalent chromium is the principal form of chromium found in food and supplements. It is ubiquitous in nature, occurring in air, water, soil and biological materials. Hexavalent chromium compounds are toxic, mutagenic and environmental contaminants and are only rarely found in food.⁴⁵ Still, some foods contain high levels of other chromium compounds, e.g. yeast, black pepper and raw sugar.⁴⁶ The intake from non-food sources of chromium, such as cooking utensils and electric kettles have been reported to show an increase of chromium release when cooking acidic food products in stainless steel utensils.^{47,48,49} Such low level contamination of food during processing and cooking has been considered as a probable source for Cr in the diet.⁵⁰ Most recent evidence strongly supports the conclusion that there is only a diminutive fear of toxic reactions from trivalent chromium consumption via food.⁵¹

Mo:

Molybdenum occurs in all foods, but at very low levels, usually less than 1 mg/kg. The major sources of molybdenum are cereals, milk, dairy products and legumes.⁸ Molybdenum in food is readily absorbed by the body. More than 80 % is absorbed in the stomach and the remainder in the small intestine.⁵² Retention rates are low and most of the metal appears to be excreted in urine within a few hours. A British expert group concluded that there are insufficient data from animal and human studies to establish a safe upper level for molybdenum⁵³ and it has not attracted much attention from health authorities or legislators as a contaminant of diets.

W:

Tungsten appears to have very low acute toxicity and is considered relatively nontoxic even when consumed in large amounts.⁵⁴

Co:

There is also only limited information on levels of cobalt in food products, but some reported values show low contents of Co (below 0,1 mg/kg).⁸ Cobalt intakes higher than normal are reported for beer drinkers in 1968, because of the use of cobalt salts as an additive to improve the foaming quality. The syndrome "beer drinker's cardiomyopathy" was characterized by pericardial effusion, elevated hemoglobin concentrations, and congestive heart failure. The intake was estimated to be 6-8 mg pr. person daily.⁵⁵ Cobalt is an integral part of vitamin B12 and such injections administered to allergic individuals may produce a red, tender and itchy area around the site of the injection, just as oral ingestion of vitamin B12 is known to cause intractable hand eczema for some patients.⁵⁶

2.3 Legislation and regulations

Food contact metals and alloys are regulated by the European Commission Framework Regulation (EC) 1935/2004,⁵⁷ which simply states that food contact materials shall be safe. It is stated that contact materials shall not transfer components into the food in quantities that could endanger human health, change the composition of the food in an unacceptable way, or deteriorate the taste and odour of foodstuffs.

Overall migration tests are described in the EC Directive 85/572/EEC, where the principle is that non-volatile substances from a sample of the food contacting material (often plastics) is determined as the mass of the residue after evaporation of the food simulant. The food simulants to be used in migration tests with a particular food product are described in the annex of EC Directive 85/572/EEC, where it is suggested to use one of the following simulants:

- distilled water or of equivalent quality.
- 3 wt.% aqueous acetic acid.
- ethanol 15 wt.% in aqueous solution.
- olive oil.

Producers and importers of materials and food products have a responsibility for securing that the materials they sell, import or use obey the laws given above. The companies involved must have their own documentation to show this. Guidelines concerning materials intended to come in contact with foodstuffs are given in a more technical document made by the Council of Europe's Policy Statements.¹³ The responsible food producing company should evaluate its processing equipment according to such guidelines available at the web page of EU's European Food Standards Agency, EFSA.⁵⁸ Additionally guidelines are given as e.g. BgVV in Germany or by FDA administrating legislation regarding materials intended for food contact in USA. If materials are accepted by German or American legislation it is normally accepted in Europe.

Limit values for lead, cadmium, mercury and tin are given, regardless if the source of metal contamination is due to the natural content or as a consequence of processing or storage.⁵⁹ In Denmark, if suspicious metal contents are found by the authorities it must be further evaluated according to Danish law.⁶⁰ At present time no specific rules are given for control of metal release from materials used for processing, however the EU Framework Regulation no. 2023/2006 from December 2006 concerning good manufacturing practise for materials in contact with food will be applicable from august 2008. This regulation aims for safe manufacturing by use of adequate materials and processes and to secure that the company producing or importing these materials has established a quality and document control system.

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3. Introduction to corrosion, wear and tribocorrosion

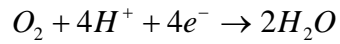
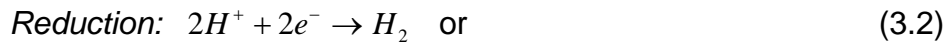
It is necessary to introduce basic wear and corrosion theory in order to understand the variety of parameters affecting the studied material degradation types. This section is by no means a comprehensive description of corrosion and wear, but only a short introduction of important denotations and principles. Section 3.1 gives a short introduction to corrosion and corrosion testing and section 3.2 introduces important wear principles. Section 3.3 introduces the concept of tribocorrosion with focus on sliding wear and erosion-corrosion.

3.1 Corrosion

Processing of food products often require corrosion resistant materials. Important parameters limiting the life time of process equipment are low pH, high salinity or process conditions as high temperature, pressure or exposure to mechanical wear. Stainless steel is a widely used material in the food industry and is generally resistant to corrosion, but corrosion can still occur for stainless steel and other materials, if they are used outside their design specifications or poorly maintained. Reported cases of corrosion in the food industry are summarized in appendix 1.

Before implementing new materials in processing equipment, corrosion tables, datasheets, and similar references can be consulted and corrosion tests in laboratory can be performed using methods as described later in section 5.1. Laboratory tests used to study metal release from processing equipment can be performed in a simulating media or in the real food product. There can be quite a difference between proper pH- and chloride -simulating test solutions and the real food product, since parameters as viscosity or multiple phases can have great importance on the aggressiveness of the media. Also biofilm and adsorbed proteins are of great concern in the food industry.⁶¹ If adsorbed proteins are not properly removed by cleaning, it will increase the risk of deposit corrosion and introduce hygienic problems, since adsorption of proteins is considered the first step of the mechanism leading to biofilm formation.⁶²

When a metal corrodes in aqueous solution an oxidation and a reduction process will take place depending on the electrochemical potential of the metal in the actual environment and parameters as e.g. oxygen concentration and the pH-value. Examples of such processes for iron are:



The mixed potential between the equilibrium potentials for the oxidation and reduction processes describes the potential of the total corrosion reaction and is denominated the open circuit potential.

The thermodynamics for corrosion reactions of elements can be illustrated in Pourbaix diagrams, showing the equilibrium potential dependence of pH, based on Nernst equation, at given pressure, temperature and concentration. Pourbaix diagrams can be a useful tool, as the thermodynamic possibilities of active corrosion, immunity of passivity can be predicted. Nevertheless the kinetics of corrosion reactions can not be determined by Pourbaix diagrams and must be found using experimental techniques. An important parameter in this context is the overpotential. An applied overpotential forces the system away from its equilibrium potential and as a result current flows in the system. The working electrode is then referred to as being polarised. The total overpotential can be separated into parts due to solution resistance, charge-transfer reactions, crystallisation, reaction and diffusion taking place at the electrode solution layer.

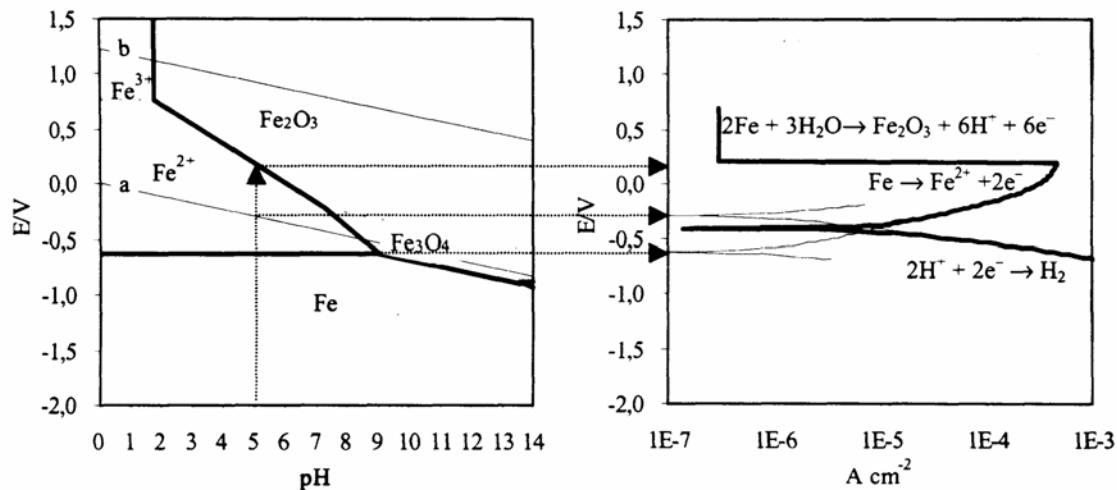


Figure 3.1 Pourbaix diagram for Fe with an activity of 10^{-6} and H_2 , O_2 activities = 1 (left) and a schematic polarization curve for iron (right). The curves for hydrogen ion reduction and iron oxidation are indicated together with the sum curve.⁶³

Figure 3.1 shows how iron can passivate at an overpotential and thus decrease the corrosion rate. For stainless steels such a passive layer is composed of various

chromium and/or nickel and iron oxides that exhibit different electrochemical characteristics than the underlying alloy. If this passive layer is damaged (mechanically or electrochemically) while in an aggressive environment, active corrosion of the freshly exposed surface will occur.

Electrochemical methods allow for rapid and precise corrosion rate measurements and may be used to measure the corrosion rate in systems that cannot be visually inspected or subjected to weight loss tests. The connection between electrical charge; current (I) multiplied by time (t), and mass transferred in an electrochemical reaction (m) can be described by Faradays law using the elements molar weight (M) and Faradays constant (F).

$$m = \frac{M \cdot I \cdot t}{z \cdot F} \quad (3.3)$$

This simple equation makes it easy to convert corrosion current densities into corrosion rates, but the current can only be used as an approximate quantification of metal dissolution. If there is an ohmic drop in the system or side reactions are taking place, e.g. oxygen or hydrogen evolution, passivating reactions or reactions of organic species in the environment, the current will not describe the actual metal dissolution rate. In many tribocorrosion setups the cell geometry differs from the standardized corrosion cell, thus the electrochemical conditions are less defined. For example, shielding effects by a moving counterpart exposing the working electrode to wear can cause an ohmic drop between the working and reference electrodes, meaning that the actual electrode potential, E , differs from the applied potential, E_{app} .

$$E = E_{app} - I \cdot R \quad (3.4)$$

Here R is the effective electrolyte resistance between the working electrode and the reference electrode and I is the current. If an ohmic drop is present in a tribocorrosion setup the influence of wear on the tribocorrosion behaviour of different materials can only qualitatively be evaluated from the obtained data.

Polarization

By polarising the working electrode anodically and cathodically, straight Tafel lines can be drawn into the polarization curve and extrapolated back to their intersection giving the corrosion potential and current. Performing polarization curves are quite

disturbing to the free corrosion situation. The dynamic change in potential may induce gaseous evolutions, passivation or local corrosion phenomena describing the behaviour of the material, but if curves are incorrectly analyzed they may give misleading interpretation of the material behaviour in industrial systems.

Chronoamperometry

Chronoamperometry is a static electrochemical technique, where the potential of the working electrode is fixed (possibly stepped) and the resulting current is monitored as a function of time. The technique can be used to approximate metal loss, if the reactions are assumed to be faradaic processes occurring at the electrode by applying equation 3.3. The technique has proven to be easily applicable in the tribocorrosion setups described in section 5. The principle in chronoamperometry is that a potentiostat establishes a fixed electrochemical potential between the working electrode and the reference electrode. The resulting current between the auxiliary electrode and the working electrode is then measured giving the corrosion current. A limitation of this electrochemical technique is that it needs a fixed potential value, which can be difficult to set realistically. When compared to monitoring of the electrochemical open circuit potential, chronoamperometry offers a lot more information, especially the possibility for approximate quantification of material loss.

Electrochemical Impedance Spectroscopy

The electrochemical impedance spectroscopy (EIS) technique uses an ac-signal to polarise the electrode around the corrosion potential at small amplitudes (10 mV) while impedances are studied. To interpret the impedance data the system is modelled by an equivalent circuit. The simplest circuit for modelling corrosion is Randles circuit as given in figure 3.2.

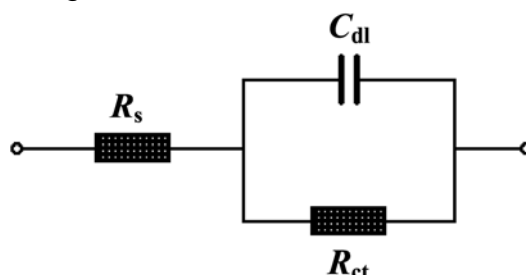


Figure 3.2 Randles circuit where R_s is the solution resistance, R_{ct} the charge transfer resistance and C_{dl} the double layer capacitance.

The electrolyte resistance (R_s) depends on the electrolyte properties and should be equal for surfaces with the same surface area and in the same electrolyte. The

interface of a metal in an electrolyte can be envisioned as a layer of ions being adjacent to the electrode surface with a layer of solvated ions further away from the surface. The two layers of ions can be simulated as a capacitor since they store charge, thus called the double layer capacitance (C_{dl}). The charge transfer resistance (R_{ct}) describes the resistance of reactions as e.g. given in equations (3.1) and (3.2). The Randles circuit represents the simplest modelling of corrosion, but additional components can be added representing diffusion, adsorption, film pores etc. The EIS theory and techniques are described in more details elsewhere.⁶⁴

3.2 Wear

Only a few cases of material failure in the food industry caused by wear (without the influence of corrosion), have been reported in literature. Presumably many process equipment breakdowns are not thought of as failures, but as simple material maintenance and parts are being replaced without further questioning of the cause of material degradation. Most often the production line is designed to avoid severe wear, but it is difficult completely to avoid wear in processing equipment as tubing/piping, pumps, valves, homogenizers, ingredient feeders, blenders, mixers or conveyers. In this work two groups of wear types will be treated in detail; sliding wear contact between equipment components resulting in adhesive or abrasive wear and erosive wear due to the processing flow velocity and possible particles in the food product.

Friction and wear are caused by the interactions between surfaces in mechanical contact and sliding against each other. The characteristics of these interactions are a result of the materials involved, the geometrical and topographical characteristics of the surfaces, and the overall conditions under which the surfaces are made to slide against each other as; loading, temperature, humidity, chemical environment, type of contact, etc. All mechanical, physical, chemical, and geometrical aspects of the surface contact and of the surrounding atmosphere affect the surface interactions and thereby also the tribological characteristics of the system. Therefore, friction and wear can not be predicted from simple materials parameters, but require unique characterisation of the whole tribological system. The aspects surrounding a wear situation that should be considered for simulation has been grouped into seven broad categories.⁶⁵ There are many elements in each of these categories which have to be considered and these can vary with the situation. Figure 3.3 provides a summary of some of the typical elements considered in these categories.

Category	Typical Aspects to Be Considered
Materials	Composition, processing conditions, cleaning, surface preparation, sources, coating thickness
Geometry	Line, point or area contact, size, roughness conditions
Motion	Rolling, sliding or impact, unidirectional, oscillatory
Loading	Constant, fluxuating, impact, contact stresses, uniformity
Lubrication	Lubricated or not, solid, grease or fluid, composition and properties, amount, supply, aging, breakdown, boundary
Environment	Temperature, relative humidity, gaseous and particulate composition, abrasive, corrosive, fluid flow characteristics
Heat dissipation and generation	Heat conduction paths, source of heat, cooling, specimen thickness, surface temperatures, flash temperatures

*Figure 3.3 Simulation categories.*⁶⁵

When considering the microscopic interaction between surfaces in contact, the area of real contact is much smaller than the nominal contact area. The applied load is carried by a number of small local asperities making up the area of real contact, and wear behavior results from the interactions between these local contact asperities. Microscopic welding and subsequent rupture can occur and is termed adhesive wear. A severe form of adhesive wear is galling, resulting in material transfer being macroscopically visible. The properties of a material in the real contact areas may be far from those measured in normal mechanical testing procedures, and the coupling between wear properties and traditional mechanical properties, such as elastic modulus and yield strength, is weak.^{67,68}

In situations involving sliding contact, a companion term with wear is friction. Friction is the force that occurs at the interface between two contacting bodies and opposes relative motion between those bodies. Generally, the magnitude of the friction force is described in terms of a coefficient of friction, μ , which is the ratio of the friction force, F_t , to the normal force, F_n , pressing the two bodies together.

$$\mu = \frac{F_t}{F_n} \quad (3.5)$$

Distinction can be made between the friction force that must be overcome to initiate sliding and the force required to maintain a constant relative speed. The coefficient associated with the former is usually designated the static coefficient of friction, μ_s , and the latter the dynamic or kinetic coefficient of friction, μ_k . Given the insight, how complicated a surface contact consists of interacting local asperities, makes it understandable that modelling of friction and wear becomes very difficult. This lack of good models strongly complicates the interpretation of measured wear and friction

data. There is also no simple correlation between wear and friction; for example, low friction does not automatically imply low wear rates.⁶⁹

Tribological test methods can be classified according to their degree of realism, i.e., how closely they imitate the conditions of a real application. Generally a high degree of realism is aimed for, but there are also many reasons for evaluating materials in tests further away from application, as e.g. cost, test time, the accurate control of test conditions, or the wish to perform a scientific study of individual, isolated wear mechanisms. With such simple model test a large range of materials can be rapidly and easily evaluated, under well-controlled test conditions. The degree of realism and the possibility of making reliable conclusions about performance or usability in an application decrease, when going from field testing to simpler model testing.⁷⁰

Wear of non food contact materials can be minimized as in any other processing industry by appropriate maintenance and lubrication. For materials in contact with food, external applied lubrication is not always an option. Since processed food products can be rather aggressive, corrosion and wear occurring simultaneously have been investigated using tribocorrosion techniques allowing for monitoring of combined wear and corrosion. A description of tribocorrosion and laboratory techniques reported in literature, used for investigating tribocorrosion behaviour of materials during erosive or sliding wear is described in the following.

3.3 Tribocorrosion

Tribocorrosion is an important material degradation mechanism to study when investigating metal release into food products, since food products are potentially aggressive and because of the inevitable mechanical interactions taking place during processing. Tribocorrosion can be defined as degradation of material surfaces subjected to combined action of a mechanical loading and a corrosive environment.⁷¹ The synergy resulting from coupling mechanical and environmental effects can cause larger material degradation than expected, if testing the two degradation processes separately. A description of tribocorrosion presented by Watson et al.⁷² describes the total material loss as the material loss due to corrosion together with the material loss due to wear, but then added an extra material loss due to a synergy effect interacting between corrosion and wear. This synergy can be split into parts of increased mechanical wear due to corrosion or an increase of corrosion due to mechanical wear.

$$T = C_w + W_c = (C_0 + S') + (W_0 + S'') \quad (3.6)$$

The total material loss is termed T , which can be found as weight loss. The corrosion of samples with and without exposure to wear is termed C_w and C_0 respectively. Wear influenced by corrosion W_c is determined as the difference between T and C_w . The ASTM standard G 119 suggest that W_0 is found by cathodically protecting the specimen, and with a determination of C_0 it is then possible to isolate the two components of synergy; S' as the increase in corrosion due to wear and S'' as the increase in wear due to corrosion.

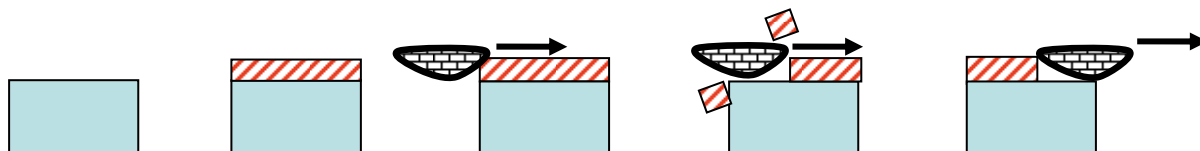


Figure 3.4 Illustration of tribocorrosion (e.g. erosion-corrosion) occurring on passivating materials. A passive layer is formed and an abrasive particle removes the passive layer, exposing the bulk material for accelerated corrosion. The surface might repassivate as the solid particle abrasion stops, but the coexistence of corrosion and wear has increased material loss more than if the degradation mechanisms occurred separately.

The increase in corrosion as a consequence of wear can be caused by removal of passive layers as illustrated in figure 3.4. In such a case it can be misleading to determine W_0 by means of cathodic protection, since it will change the material surface properties by electrochemically eliminating the passive film. In worst case cathodic protection can cause hydrogen evolution, which can affect the wear contact and possibly cause hydrogen damage to the specimen, such as e.g. hydrogen embrittlement for certain steel types. The synergy effect describing increased mechanical wear due to corrosion can occur, if corrosion products are released and then act as third body wear particles. More obvious is the case where a wear-resistant coating is corroding and thereby exposing the bulk metal to wear. Finally, a negative synergy effect as a consequence of combined corrosion and wear might occur. This phenomena has been reported when investigating the influence of handling on nickel release from euro coins (see appendices VI and VII).^{73,74}

3.3.1 Erosion-corrosion

Erosion-corrosion is a sub-group of tribocorrosion and the mechanism for this synergy is recognized as a severe problem in industrial processes as well as outside the food industry. It has been ranked the fifth most important degradation mechanism

in the offshore and chemical sectors.⁷⁵ Examples of erosion-corrosion failures in the food industry are described elsewhere^{76,77} (Appendix I). The following describes results from literature concerning erosion properties of materials and techniques used for investigating erosion-corrosion.

Wear caused by hard particles bombarding a surface is called solid particle erosion. A distinction between abrasion and solid particle erosion is that the latter refers to a series of particles striking and rebounding from a surface, whereas abrasion results from sliding of abrasive particles under the action of an externally applied force, as in e.g. sliding wear situations.⁸⁰ Erosive wear can involve both plastic deformation and brittle fracture, and the details of the wear mechanism depends on both the material, the eroding particles and the condition of the impacts, primarily particle mass, velocity, and impingement angle. The erosion behavior of materials is closely linked to such a range of parameters as summarized in table 3.1.

Tabel 3.1. Erosion-corrosion parameters.

Material	Particles	Environment
Composition	Composition	Composition
Design	Size and shape	Temperature
Corrosion properties	Density and hardness	pH
Hardness and ductility	Velocity	Flow properties
Topography	Concentration	Viscosity
Microstructure	Angle of impact	Conductivity

In order to understand predominating degradation mechanisms in a given system each parameter effect on the total degradation must be evaluated independent of each other. This also includes quantifying degradation parts due to corrosion and erosion alone or due to synergistic effects.

As regards erosion alone, the effect of impact angle has been studied and found fundamentally different for materials with different mechanical properties. The erosion rates of brittle materials generally increase with increasing impact angle. Ductile materials, however, tend to erode the fastest at an intermediate impact angle, often at around 20 to 30° measured from the eroded surface tangent.^{81,82,83} Exceptions can be found, especially if particles are spherical,⁸⁴ and the opposite relationship has been proven for spherical particles impinging a ductile surface with highest material losses at high angles.⁸⁵

Another classical result from literature is the decrease in degradation rate with increasing material hardness as shown in figure 3.5. The erosion rate increases with the speed of the eroding particles and their masses and tends to fall with the hardness of the particles, although the hardness dependence may be weak for certain groups of materials.⁸⁶

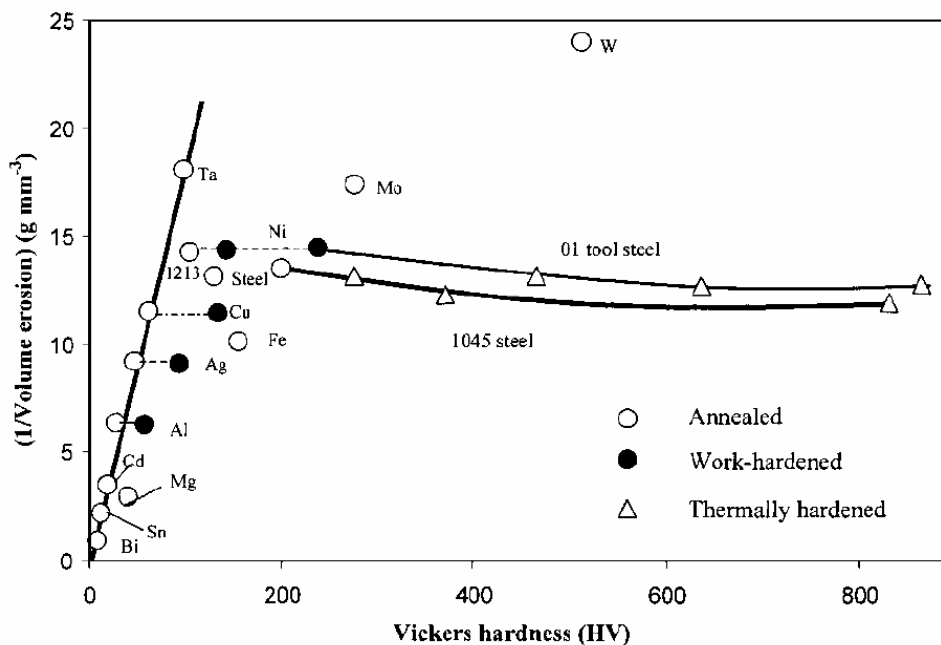


Figure 3.5. Erosion resistance as a function of hardness for massive metals and steels.⁸¹

As shown in figure 3.5 a linear relationship between erosion resistance (dry) and hardness does not exist for the mentioned steels. One explanation can be the increased velocity for an erosive particle impact as compared to the impact of a diamond used in a hardness measurement. An improved relationship has been found when hardness measurements have been performed after erosion testing.⁸⁷

As mentioned earlier a material like stainless steel is often used in the food industry because of its high corrosion resistance, but due to its poor tribological properties there is a risk of material degradation, when exposed to combined corrosion and wear. Therefore the existence of abrasive particles (pips from the vegetable itself or contaminants, e.g., grits from harvesting) are likely to influence, not just wear properties, but also corrosion properties of such materials used for process equipment. In literature it has been shown that erosion with hard particles makes stainless steel more susceptible to pitting because of increased formation of metastable pits during erosion.⁸⁸

In order to examine such phenomena erosion-corrosion setups allowing for online electrochemical monitoring can be used. Several techniques are described in literature for investigating erosion-corrosion at laboratory level. Examples are pipe flow investigations or slurry tests, where either the specimens or the slurry is rotated in a container. A slurry wear apparatus has been used for investigating wear and corrosion of mining and mineral processing equipment as pumps, elbows, tee junctions, valves, flotation cells and hydrocyclones.⁸⁹ More recently jet impingement equipment has been developed for laboratory testing where an ejector nozzle is used to entrain particles from a sand bed into a stream of water to form a slurry.⁹⁰ The use of such equipment has given the foundation for developing erosion-corrosion maps indicating regimes of erosion and corrosion dependant on parameters as material, environment, velocity etc.^{91, 92}

The slurry testing techniques are easy to use and results for ranking materials can rapidly be obtained. Draw backs are the lack of control of important parameters as particle concentration, collision velocity and impact angle between particles and the specimen. In literature there has been some discussion of the value of erosion-corrosion jet impingement setups for studying the intrinsic erosion–corrosion resistance of thin coatings or modified layers, because of the influence of the substrate.⁹³ The ratio of particle diameter to coating thickness should be as small as possible if particle erosion is to be used for evaluating coating properties.⁹⁴ Finally the total material loss should be quantified precisely, either by weight loss or topographical measurements to obtain the exact distinction between erosion, corrosion and synergy parts. When comparing different surface modifications on the same substrate the test setup can give reliable data, useful for development of wear resistant stainless steel surfaces providing on-line information on the corrosion resistance (see Appendices IV and V).

3.3.2 Sliding wear in aggressive environments

Wear and friction in sliding contacts are of great interest because of their common occurrence in many machine elements. Sliding wear does not specify a wear mechanism, but refer to the type of contact between two surfaces in relative motion. Numerous types of material removal mechanisms may appear in this type of contact. Surface damages or wear based on adhesion or on surface fatigue are common, but also grooving by surface asperities, abrasion and other mechanisms are possible. Numerous tests for sliding and rolling wear evaluations have been produced and are

specified in national standards, e.g. block-on-ring (ASTM G77), crossed cylinders (ASTM G83), pin-on-disk (ASTM G99) or sphere-on-disk (DIN 50 324).⁹⁵

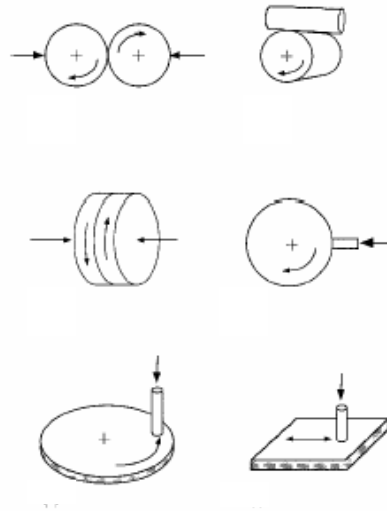


Figure 3.6 Illustration of common sliding wear test configurations.⁹³

Because of the variety of surface interactions and types of surface damages that may occur in sliding contacts, only minor alterations in the test conditions can lead to radical changes in the dominant wear mechanisms and the associated wear and friction values. When choosing model tests for materials ranking, it therefore becomes important to simulate the conditions of the application in detail. Contact stress, thermal conditions, sliding speed, and chemical environment are all vital test parameters, when determining sliding wear material properties.

The interpretation of sliding wear test results is generally much more difficult than for erosion. While the type of wear by hard particles is the result of a very large number of microevents, a sliding contact may initiate a variety of interacting phenomena whose character changes as the test proceeds. As a consequence, wear rate is often not proportional to the sliding distance, and correlations to any bulk materials properties, such as hardness, toughness, etc., cannot generally be taken for granted.⁹³

When two solid surfaces are sliding against each other there will always be some distortion of each of them. When brought into contact they will initially touch at either a point or along a line. Deformations may be purely elastic or may involve some additional plastic changes in shape. With the application of load, elastic deformation enlarges these into contact areas across which the loads are distributed as pressures. The first analysis of this situation was presented by Heinrich Hertz in 1881

predicting that stresses developed in conditions of nonconformal contacts can be among the most severe in any mechanical device. The situation of a Hertzian contact is of particular interest because the most heavily loaded elements of a material, and thus the site of initial plastic yielding, lies not at the surface but a small distance beneath it.⁹⁸ Figure 3.7 shows the contours of maximum shear stress under a line contact in a material with Poisson's ratio 0.3.

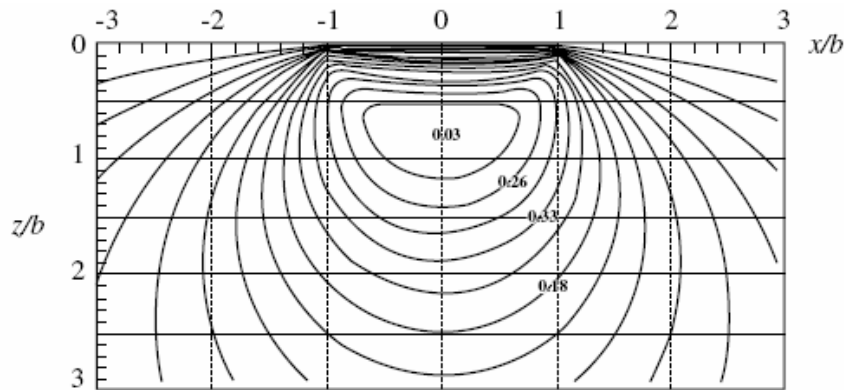


Figure 3.7 Contours of maximum shear stress normalized by Hertz stress beneath nominal line contact in a material with Poisson's ratio 0.3. The coordinates x and z are divided by the contact area b .⁹⁶

The combination of corrosion and sliding wear conditions has been extensively studied and reported in literature, using different experimental setups for controlling mechanical conditions, mainly ball-on-plate or pin-on-disc setups. Such setups with alumina parts sliding against passivating materials in sulphuric acid environment have been a simple model system for many experiments investigating tribocorrosion behaviour.^{101,102,103} Also micro tribometer setups have been used to investigate tribocorrosion behaviour of materials during sliding wear.^{104,105}

In spite of extensive laboratory work in this area, using highly controlled mechanical and electrochemical conditions far from materials and environments used for any industrial applications, it has recently been stated that the chemo-mechanical mechanisms of tribocorrosion still are incompletely understood and that there is a strong need for standardized accelerated tribocorrosion test methods in this area.¹⁰⁶

In the food industry only a few cases of sliding wear failures are reported,^{107,108} presumably because direct wear to wear contacts often are prevented by design. A case where it is not directly possible to avoid sliding wear is in the production of minced meat. In this process the meat enters a conveyor screw and is processed through a perforated disc by rotation of knives in sliding contact with the disc. In this

work a block-on-ring test setup has been used to simulate this situation, because it provides the sliding wear conditions necessary for simulating degradation of parts used in the meat mincing industry (Appendices II and III). The use of such a block-on-ring tribocorrosion test setup has given insight in corrosion-, wear- and synergy-parts of metal degradation taking place and evaluation of the tribocorrosion behaviour of new materials that are now being tested a full scale in the industry.

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4. Wear and corrosion resistant materials and surfaces

A short introduction to common materials and surface modifications used in the food industry are given together with a description of innovative ways to obtain materials with improved corrosion and wear properties.

4.1 Materials

Stainless steels are alloys of iron and chromium with or without other added alloying components. The essential requirement to confer the expected minimum passivating characteristics on a stainless steel is a chromium content of not less than 13 wt.%. To modify passivating characteristics or manipulate metallurgical structures the relative stabilities of austenite and ferrite can be varied. Carbon, nickel, manganese, nitrogen, and copper stabilize austenite; chromium, molybdenum and silicon stabilize ferrite.

Austenitic stainless steel is much used because of its easy machineability and corrosion resistance. It can be recognized as being nonmagnetic at room temperature, yet parts of the metastable austenite temperature will be transformed into martensite if heavily deformation hardened. Standard austenitic steels, such as AISI 304 and AISI 316 are supplied by the manufacturer with the carbon retained in supersaturated solution by rapid cooling from a final heat-treatment at 1100°C, and they are intended to be used in this condition. If they are subsequently reheated and cooled slowly through a critical temperature range, they can become sensitized, a condition in which they are susceptible to intergranular corrosion, i.e., corrosion along the grain boundaries. Intergranular corrosion due to sensitization in the heat-affected zones close to welds is known as weld-decay. The stainless steel L types have low carbon contents and can be used for welding purposes. The effect of sensitization and its suitable countermeasures are well-known and usually pose no problem to those who are aware of them.¹⁰⁷

In filtration, evaporation and spray-drying plants, various combinations of higher temperatures, higher pressures, diminished solubility for oxygen, higher concentrations of e.g., chlorides in feed fluids or oxygen starvation under deposits can produce environments that are too aggressive for AISI 304 steels and must be resisted by using the more expensive molybdenum-bearing austenitic steels, AISI 316 or AISI 316 L. One particular environment that is too aggressive for even AISI 316 is the intermediate liquor obtained after treating with hydrochloric acid to recover

proteins in dairy production.¹⁰⁸ Alternative materials are Duplex steels or SMO grades.

Massive materials used in the food industry for wear applications are chromium containing tool steels as Sverker 21, Stavax or similar. These materials are not always the most appropriate materials, but nevertheless they are still used for many processing applications in the food industry. If in contact with aggressive food products or used under severe wear conditions Co based materials with superior mechanical properties can be used as e.g. Stellite®. Besides Co, Stellite® has a high amount of Cr (up to 30%) and W (up to 5 %). Stellite® is difficult to machine, but can be applied by thermal spraying or PVD processes. Table 4.1 summarizes investigated materials, ranging from low alloyed hardenable steel (80CrV2) to expensive highly alloyed wear and corrosion resistant materials (Stellite®, Nicrofer®).

Table 4.1 Composition of selected materials typically used in food processing equipment and investigated in this work.

Material	Fe	Cr	Ni	Mo	Mn	Si	C	V	Co	W	N
AISI 316 L	68,9	16,7	10,1	1,9	0,9	0,4	0,03	0,1	-	-	-
Stavax	rest	13,6	-	-	0,5	0,9	0,4	0,3	-	-	-
80CrV2	rest	0,5	0,1	-	0,4	0,3	0,8	0,2	-	-	-
Sverker 21	rest	11,8	-	0,8	0,4	0,3	1,6	0,8	-	-	-
HSS	rest	4,0	0,3	4,9	0,2	0,4	1,7	1,8	-	6,2	-
Stellite® 6	-	28	-	-	-	-	1,1	-	66,9	4	-
Vancron® 40	rest	4,5	-	3,2	0,4	0,5	1,1	8,5	-	3,7	1,8
Nicrofer® 5923	0,5	22,7	rest	15,3	0,3	0,03	-	-	0,03	-	-
Nicrofer® 3127	rest	26,5	31,6	6,5	1,5	-	-	-	-	-	0,2

4.2 Surface modification

Surface hardening in general involves many processes to improve the wear resistance of parts while utilizing the interior properties of the bulk steel. This section is limited to give the background for surface modifications using nitriding treatments and physical vapour deposition coatings with focus on diamond like carbon.

4.2.1 Nitriding

The poor tribological behaviour of austenitic stainless steels has been described as a barrier to their wider application under tribocorrosive conditions.^{109,110} Consequently,

the development of new technologies to enhance the wear resistance of stainless steel surfaces without losing their attractive 'stainless' characteristics has recently attracted much interest.

Diffusion of nitrogen into metallic surfaces, nitriding, aims at obtaining higher hardness, improve wear- and fatigue resistance and to improve or at least maintain the corrosion resistance. Nitriding can be carried out by gas, liquid or plasma. Plasmanitriding is performed in vacuum with high-voltage electrical energy used to form a plasma, through which nitrogen ions are accelerated to impinge on the specimen. This ion bombardment cleans the surface, heats the specimen and provides active nitrogen. Plasma nitriding can be combined with a physical vapour deposited coating to increase its efficiency further. New thin film hard coatings like chromium nitride, aluminium titanium nitride and titanium carbo-nitride or diamond like carbon can be applied to a plasma nitrided specimen, usually in the same reactor vessel to avoid contamination and eliminate the need for extra cleaning. These are called duplex treatments and are not to be confused with Duplex steel.

In the mid-eighties it was discovered, using plasma-nitriding, that by lowering the temperature to 450°C (or lower) it is possible to dissolve large amounts of nitrogen in stainless steel without precipitation of chromium nitrides, i.e. without altering the corrosion properties of the steel.¹¹¹ This nitrogen supersaturated structure has been denoted "expanded austenite". Plasma-based processes circumvent the problem with impenetrability of the passive layer as it is continuously sputtered away during the nitriding process.

Traditional gaseous hardening treatments are carried out at relatively high temperatures (> 500 °C), but are not suitable for stainless steel grades as the corrosion properties are impaired due to precipitation of chromium nitrides (sensibilization). Furthermore, the passive layer is an effective diffusion barrier for nitrogen atoms, thus in order to nitride stainless steel by a gaseous treatment, the passive layer has to be removed. Recently, a process was developed, which makes it possible to use gaseous low temperature hardening (nitriding/carburising) in furnaces normally used for heat treatment of steels.^{112,113} The low temperature nitriding (LTN) hardens the surface of stainless steel (10-40 µm) up to 1400 HV. Figure 4.1 shortly illustrates the process.

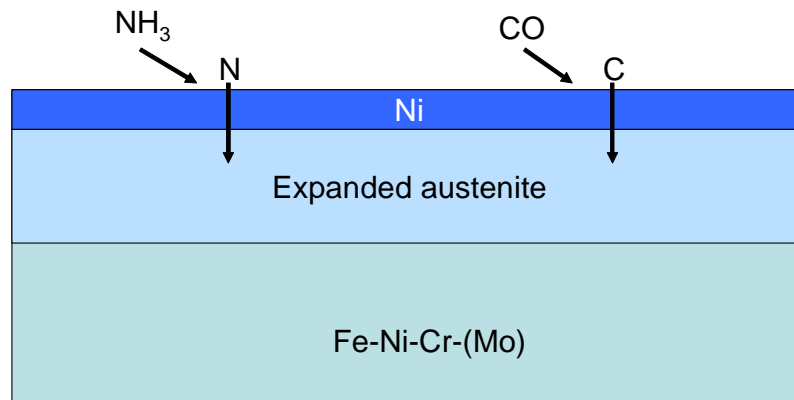


Figure 4.1 Schematic illustration of low temperature gaseous nitriding/carburising of stainless steel.

Firstly the passive layer is removed chemically or electrochemically and then an ultra thin layer of nickel (10-20 nm) is deposited before the surface repassivates. The nickel coated specimen can be carburized/nitrided in adequate composition of gases at temperatures below 450°C for nitriding and 500°C for carburising. Finally the nickel layer is removed and the passive layer reformed in diluted nitric acid.

The hardening effect is caused by interstitial solution hardening and deformation hardening caused by compressive stresses as a result of austenite volume expansion. The supersaturation of carbon/nitrogen makes the layer thermodynamically metastable and it will decompose into austenite/ferrite and carbides/nitrides, if heated sufficiently. The layer can for high interstitial contents of nitrogen be quite brittle, which can cause cracking. Investigations of the wear resistance using a pin-on-disc setup report 100 times lower material loss as compared to untreated stainless steel. It is also reported that the corrosion resistance is unaltered or improved, i.e. more noble corrosion potential, larger passive area and improved resistance against pitting,¹¹⁰ yet only a small amount of work has been published concerning the tribocorrosive behavior of low temperature nitrided stainless steel.

4.2.2 PVD-coatings

The most prevalent PVD technique is sputtering. This PVD technique is based on plasma technology, where ions are accelerated towards a target by applying a negative voltage to the target relative to the substrates. The target consists of the material to be deposited on the substrate e.g. titanium, chromium, aluminium or alloys hereof. As the plasma (often Ar) ions strike the target surface, atoms from the target will be sputtered. Some of the atoms condense on the substrate surface and

builds the material atom by atom. Various gasses added to the plasma can be incorporated in the coating and the process is then termed reactive sputtering. Sputtering from several targets can produce alloys or layered structures. Targets can consist of various elements.

So-called diamond-like carbon (DLC) coatings can be produced, if the sputtering target is made of graphite. The physical properties of DLC coatings can be similar to the ones of diamond, but the degree of similarity depends strongly on the structure and composition of the DLC coating. The types of bondings in DLC can be described as a mixture of C-C sp^3 (diamond type), C-C sp^2 (graphite type) and C-C sp^1 (the hybridized binding). Hardness and wear properties depend especially on the content of sp^3 bondings and the hydrogen content in the DLC coating. The chemical composition of the various types of C-H alloys can be illustrated in a ternary C-H phase diagram.

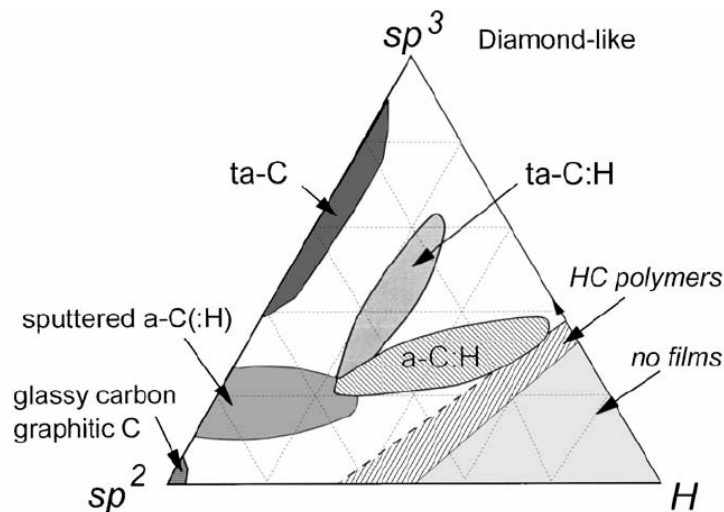


Figure 4.2 Ternary phase diagram showing the composition of various types of DLC systems.¹¹⁵

Hydrogenized DLC coatings with a mixture of sp^2 and sp^3 are denoted a-C:H (hydrogenized amorphous carbon). If the sp^3 content is increased and the hydrogen content is decreased it is possible to obtain either the ta-C:H structure (tetrahedral hydrogenized amorphous carbon) or the ta-C structure (tetrahedral amorphous carbon). The latter is the DLC type with maximum sp^3 content and a minimum of hydrogen, making it harder than a-C:H. This DLC type can be grown with deposition techniques involving high energetic ions, such as filtered cathodic arc evaporation. The DLC type called a-C:H has a H content of 20-40 at.%. Such types are usually

deposited by reactive sputtering at moderate substrate bias voltages and it is this type of DLC coatings that has been studied in this work in appendices IV and V.

Figure 4.3 illustrates the DLC coating process used in the present work. The substrate is coated with an adhesion promoting layer before the target power is increased on the carbon target. The final layer is thus deposited by sputtering from a carbon target combined with the addition of a carbon hydride gas (i.e. reactive sputtering). By this a surface mainly consisting of a-C:H is obtained.

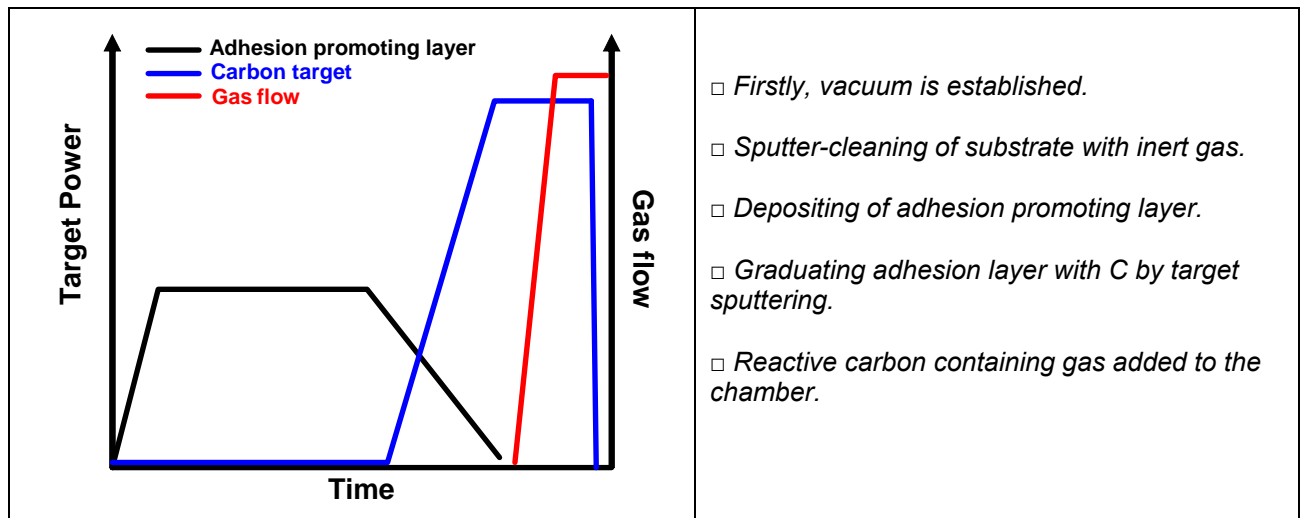


Figure 4.3 Typical depositing process of DLC.

The result is a clean stainless steel surface with an adhesion promoting layer, graduating in carbon content, and finally a reactively sputtered a-C:H layer. Such a coating system is an example of a functionally gradient coating (FGC).

Adhesion to the substrate depends on the substrate material composition, topography, pre-treatment and the deposition method and parameters used. Stainless steel can be a difficult substrate to adhere to and adhesion properties are often improved by applying intermediate adhesion promoting layers, graded or multilayered structures as CrN, TiC, SiC, Ti or TiN/TiC.^{116,117}

A cross section of a DLC coating (FGC type) on stainless steel is shown in figure 4.4.

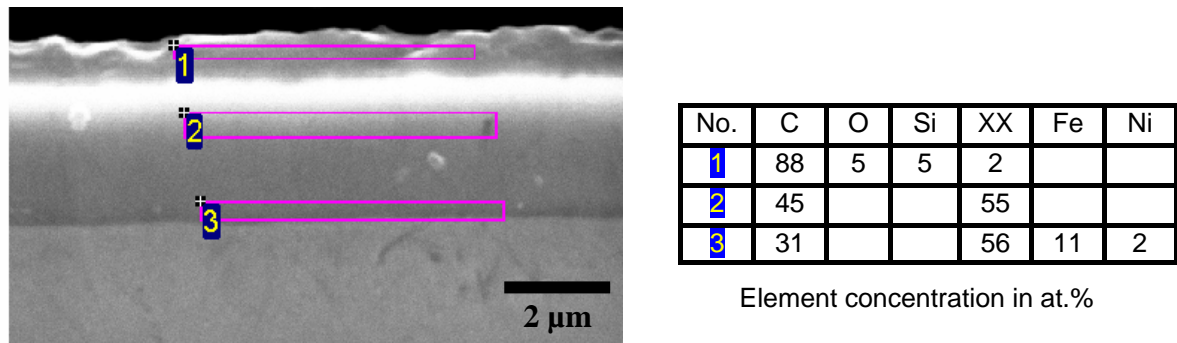


Figure 4.4 SEM image with EDS analysis of DLC coated AISI 316 L.

The thickness of the carbon graduated adhesion promoting layer is approximately 2 μm and the thickness of the DLC layer is approximately 1 μm . The EDS analysis indicates (EDS cannot provide exact elemental composition for light atoms as C) how the adhesion promoting layer (a trade secret and thus given as XX) is graduated with carbon. The EDS analysis is also likely to show a certain contribution from the underlying stainless steel substrate, explaining the Ni and Fe contribution in measurement no. 3, figure 4.4. Si and O in measurement no. 1 is possibly a contribution from the polishing or moulding material.

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5. Experimental methods

The following section describes the corrosion and tribocorrosion laboratory techniques and setups used in this work to determine combined corrosion and sliding wear or erosion properties of selected materials. Nickel release during friction from handling has been of great interest in recent literature and a setup for this purpose is presented. Results from using these experimental methods are given in appendices and in section 6.

5.1 Corrosion

Overall migration tests are described in the EC Directive 85/572/EEC, where the quantity of non-volatile substances from a sample of the food contacting material is determined as the mass of the residue after evaporation of the food simulant. A more detailed study of corrosion mechanisms not described in EC Directive 85/572/EEC can be performed with electrochemical measurements studying the corrosion behaviour of metals in contact with food products. Electrochemical measurements have been performed using cylindrical specimens ($\varnothing 10 \cdot 10$ mm) polished with SiC grit (typically to a finish of 500 or higher) and then tested in a standard corrosion cell at a fixed temperature and agitation. The potentiostats used are provided by Radiometer and polarisations are performed according to ASTM Standard G5.¹¹⁸

Materials tested in this work are AISI 304, 316 and 316 L in various juices, minced pork meat, ketchup and beverages at various temperatures. Such laboratory corrosion data have been compared with metal release in actual processing of food products during different process step as carried out in cooperation with The National Food Institute, DTU. Metal contents of samples taken before and after a juice pasteurizing process were measured with Inductively Coupled Plasma Mass Spectrometry (ICP-MS) coupled with a reaction / corrosion cell (CRC) and will be presented later in section 6.1.

5.2 Sliding wear

A block-on-ring testing facility has been modified to not just determine wear properties, but also electrochemical properties of materials during sliding wear situations. Originally the setup was used for testing oils and materials used under high loads. To ensure stabilized tribological conditions at small loads, the load applying system was changed from being pneumatic to being applied by mass. All parts holding the block and ring were modified in order to be able to perform electrochemical measurements without electrical disturbance from the tribometer (a

large steel construction). A model system consisting of an alumina ring in sliding contact with a stainless steel block in dilute sulphuric acid solution was used to demonstrate the reproducibility of the system before investigating more relevant industrial materials and conditions.

The setup, shown in figure 5.1 gives the possibility for testing of solid parts in sliding motion in accordance with laboratory procedures for block-on-ring wear testing as given in ASTM Standard G77¹¹⁹ and to monitor/control the electrochemical behaviour of the materials used.

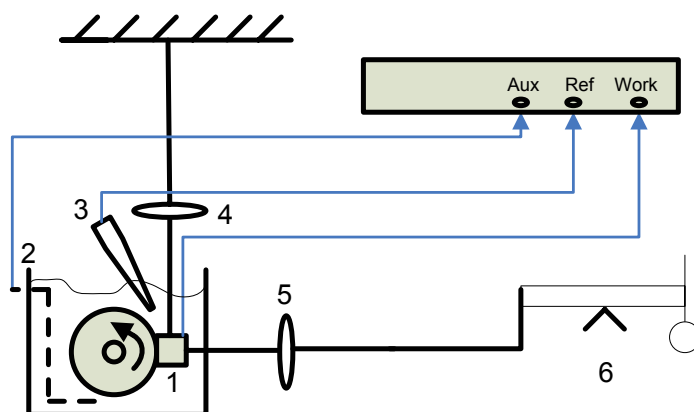


Figure 5.1 Schematic view of the block-on-ring tribocorrosion testing facility. 1. Working electrode, 2. Auxiliary electrode, 3. Reference electrode, 4. Strain gauge (Ft), 5. Strain gauge (Fn), 6. Weight load system.

Friction force, normal force, potential and current are registered during the test. The ring diameter is 35 mm and it rotates with an eccentricity below 25 μm . The use of a weight load system ensures stabilized conditions for the applied normal force.

Typical values for factors held constant throughout the tests are:

- Temperature is room temperature, 24 °C.
- Normal load (1-5 kg).
- Number of rotations (60-200 rounds pr. minute).
- All specimen were polished with SiC grit (typically to a finish of 500 or higher).
- The electrochemical potential is fixed at a certain value depending on the investigated system.

The test setup has limitations when compared to tonnage and process conditions at full industrial scale, however it gives the possibility for testing and comparing various materials and surface modifications under quite well controlled conditions. One of the drawbacks by this test method is the necessity for perfect alignment of the block and

ring. As few as possible specimens were therefore tested due to the rather time consuming process it is to set up tribological testing. Many tribocorrosion setups will have one part of the specimen surface area exposed to wear, whereas other parts of the specimen surface area are only exposed to corrosion. This can be avoided by lacquering of the surface not exposed to wear, but valuable information can be obtained by thorough examining the area not exposed to wear if refraining from lacquering. For a block on ring setup the wear track will increase with time which is a difficult controllable factor affecting the electrochemical measurements.

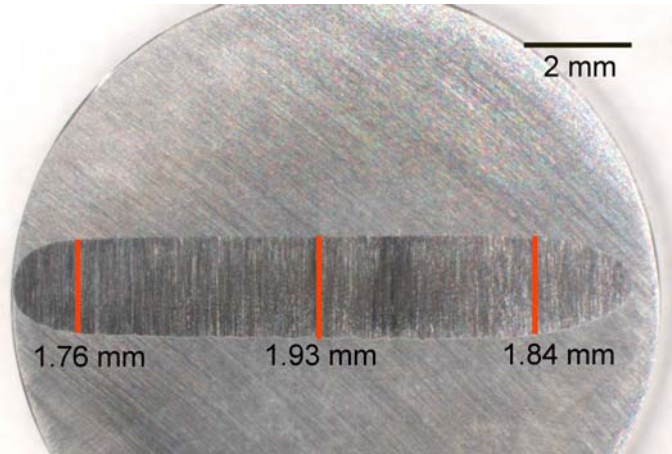


Figure 5.2 A typical wear track on stainless steel AISI 316 L after sliding against an alumina ring in dilute sulphuric acid at 15-20 N for 43 minutes.

The material loss can be determined as weight loss as well as from volume loss. The volume loss is determined from the width of the wear track (the average of three measurements as shown in figure 5.2) from the following set of equations.

$$Volume = \frac{D^2 \cdot t}{8} (\theta - \sin \theta) \quad (5.1)$$

$$\theta = 2 \cdot \sin^{-1} \frac{b}{D} \quad (5.2)$$

D is the diameter of the ring, b the average wear track length, t the width and θ as the sector angle in radians as shown in figure 5.3 with ring radius r .

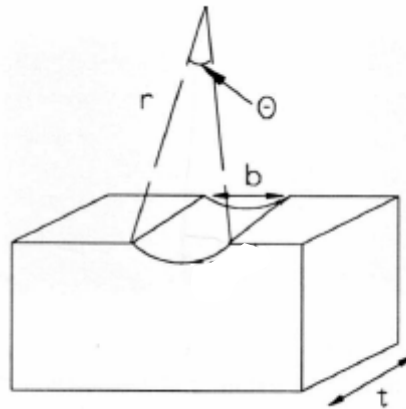


Figure 5.3 Volume loss assessment.

Materials tested with this setup are AISI 316 L, Sverker 21, HSS, 80CrV2, Vancron 40, Stavax, Stellite and alumina in mild sulphuric acid solution, chloride solution and in minced meat.

5.3 Erosion-corrosion

In order to investigate erosion-corrosion failures and to optimize materials to withstand erosion-corrosion it is beneficial to determine the material degradation caused by erosion and corrosion respectively, as well as the combined effect. A test setup allowing for electrochemical measurements under impingement with particles was built for these purposes. The design is similar to the impinging jet apparatus described elsewhere.^{120,121} The test setup is schematically illustrated in figure 5.4 and its operational principles described in appendix IV.¹²²

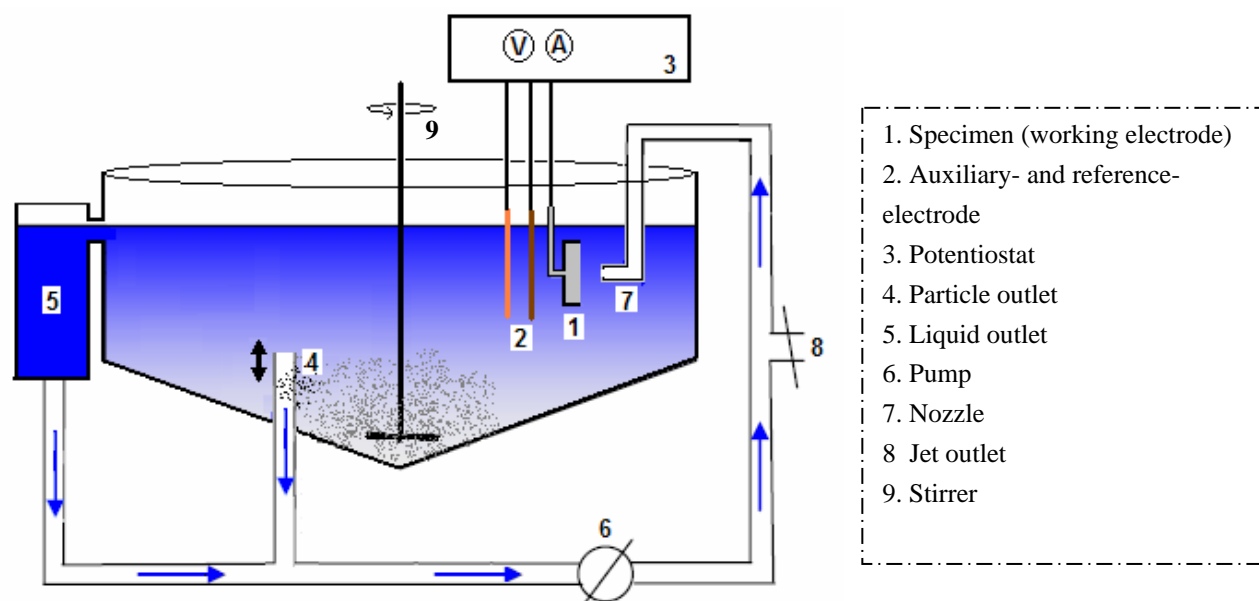


Figure 5.4 Erosion-corrosion test setup.

The erosion-corrosion setup allows specimens to undergo erosion with impinging particles, while electrochemical measurements are performed, and thus the results can be used to optimize surface properties, estimate life time of process equipment and evaluate effects of environment composition, particle concentration, fluid velocity etc. in food processing systems as well as in other processing systems.

The particle concentration is estimated by filtering 2 l samples (3 replicates) and determining the weight after filtering dry for exactly 1 minute. Weight loss of specimens before and after testing can be measured using a microbalance with a sensitivity of 0.01 mg. The reproducibility of the particle content in the jet has proven to be adequate. In literature exact values for particle distribution are often not given and therefore it has not been verified whether processing through the pump gives better reproducibility than injector types.

Samples are machined to a final dimension of $15 \times 15 \times 2$ mm and polished, appropriately cleaned, dried and weighed before testing. It is important to ensure electrical contact to the bulk of the sample material, which is done by a gold plated spring contact. Typical wear tracks are shown in figure 5.5, indicating the effect of low temperature nitriding on the resistance against pitting, as well as the increased susceptibility of stainless steel to pitting after erosion exposure.

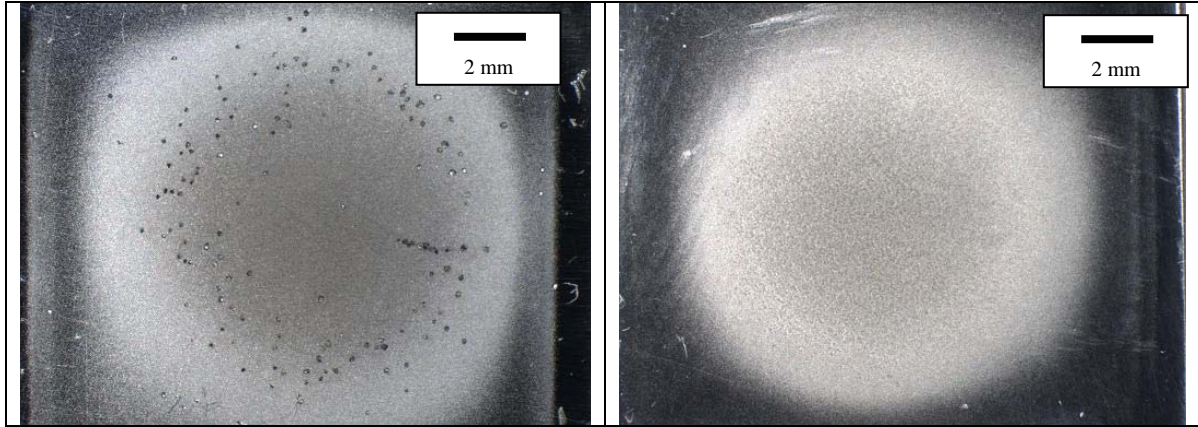
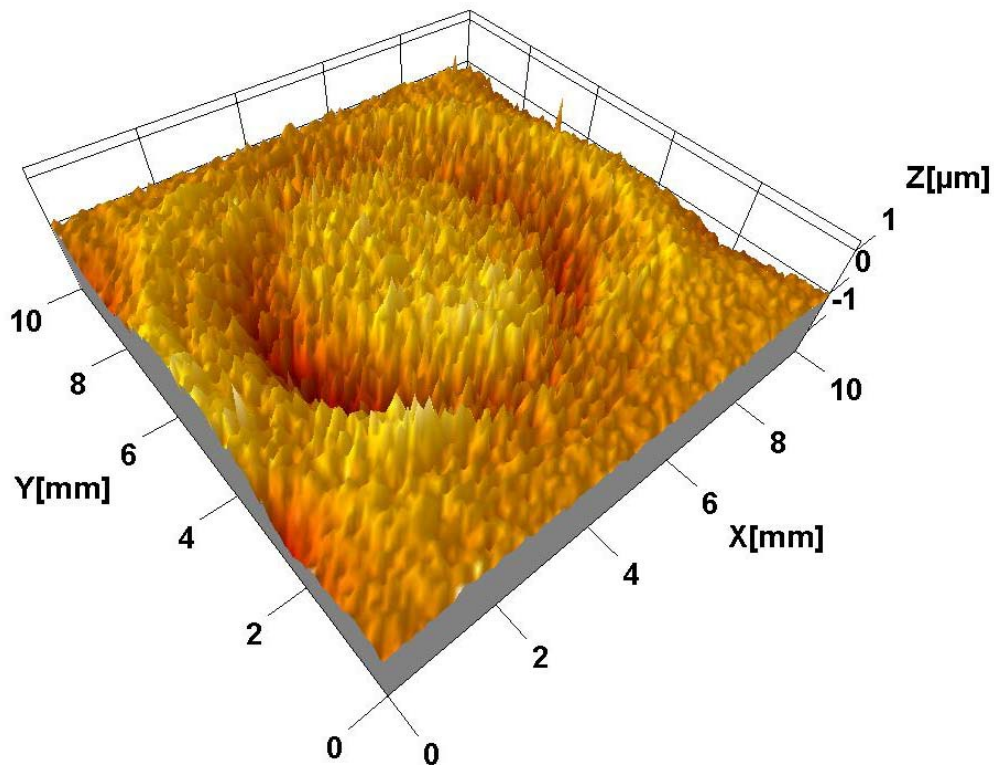


Figure 5.5 A typical wear track after erosion-corrosion of untreated AISI 316 L (left) and low temperature nitrided AISI 316 L (right). Exposure conditions 0,03 % chloride in 0,1 M natriumacetate buffer at pH 5,5 with 5,6 g/l alumina particles size 250 μm for 120 min and then the specimens were polarized to 1744 mV SHE.¹²³

The wear track has the typical flow characteristics of impinging on a flat plate at 90 degrees angle as shown in figure 5.6.



5.6 Surface topography made by nondestructive laser measurement of DLC-coated AISI 316 L after erosion-corrosion in 0.05 M sodium citrate/citric acid buffer at pH 4 with a sodium chloride concentration of 0.5 wt.% and 0.5 g/l, 250 μm alumina particles.

The hydrodynamic characteristics of impinging on a flat plate at 90 degrees angle is well-known and illustrated in figure 5.7

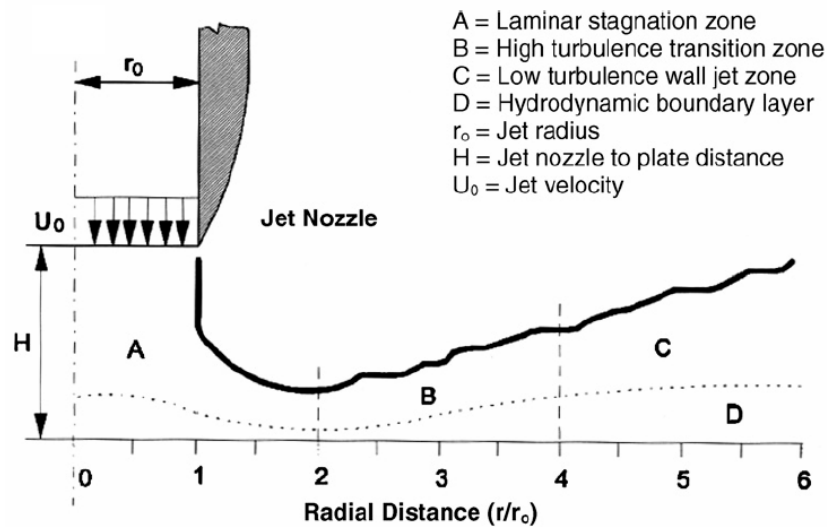


Figure 5.7 Hydrodynamic characteristics of a jet impinging on a flat plate.¹²⁴

In literature there has been some discussion of the value of erosion-corrosion jet impingement setups for studying the intrinsic erosion–corrosion resistance of thin coatings or modified layers because of the influence of the substrate.¹²⁵ Also the ratio of particle diameter to coating thickness should be as small as possible if particle erosion is to be used for evaluating coating properties.¹²⁶

Materials tested are AISI 316 L, plasmanitrided, gas-nitrided and DLC coated AISI 316 L, Stellite®, Nicrofer® alloys, Ti and Cu in food simulating chloride containing solutions.

5.4 Mild rubbing wear

A test setup has been build to investigate metal release, not focusing on food/food processing, but in general from surfaces in contact with human finger handling. Nevertheless this tribocorrosion setup also finds its relevance for investigating food contacting surfaces used in transporting, mixing or similar processes, where food products are in sliding contact with process equipment under low contact loads. The setup consists of a motor rotating a polymer disk with a radius of 10 cm. The disc is covered with synthetic washable leather. Washable leather was chosen as wearing material, while it is comparable to the situation where human skin is in contact with materials, as well as the contact load is estimated to simulate finger handling of nickel containing materials eg. coins. The motor can rotate at various speeds and

with various applied loads as determined by inserting a mass balance under the setup.

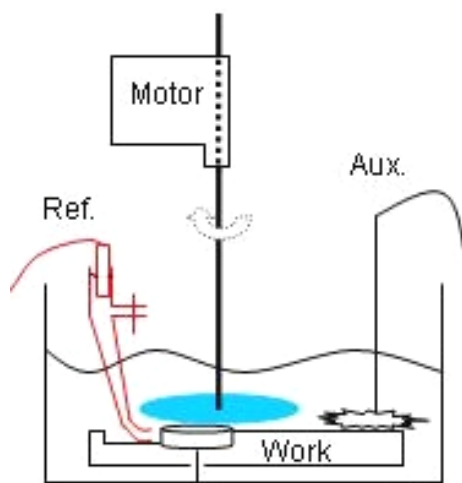


Figure 5.8 Tribocorrosion apparatus for investigating mild rubbing wear.

A standard three-electrode electrochemical setup is connected to a potentiostat. A titanium net serves as a counter electrode and a standard calomel electrode (SCE, +244 mV SHE) as a reference electrode. Samples are made of specimens 2.0 mm thick ($\varnothing 25$ mm) mounted in polypropylene with epoxy and connected as the working electrode.

As is the case for all tribocorrosion experiments the cell geometry differs from the standardized corrosion cell, thus the electrochemical conditions are less defined. Especially for this setup, it was obvious that possible shielding effects by the moving leather on top of the working electrode could cause an ohmic drop between the working and reference electrodes. Nevertheless, the effect of shielding from the washable leather was found to be negligible, since electrochemical measurements performed with and without the working electrode covered by the washable leather were identical. The setup has primarily been used to illustrate principles of tribocorrosion and for a more detailed study of metal release from handling metals. Nevertheless the method can also find its use in investigating mild wear which also takes place in the food industry. For instance, it is a clear opinion in the food industry that new grit blasted surfaces become easier to clean after a certain time of processing, suggesting that wear possibly combined with corrosion is taking place, smoothening the surface.

Mild wear tests have been performed at room temperature in a standard artificial sweat solution with the composition: sodium chloride, 0.3 wt%; lactic acid, 0.1 wt% and urea, 0.1 wt%. Ammonia solution (1%) was added to adjust the pH value to 6.50 ± 0.10 . Materials tested in this setup are AISI 316 L, Ni, NiSn, Euro alloys Cu75 Ni25, Cu75 Zn20 Ni5, the 2-euro coin itself and all Danish coin alloys.

¹¹⁸ ASTM Standard G5-94, Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements, Reapproved 1999.

¹¹⁹ ASTM Standard G77-98, Standard Test Method for Ranking Resistance of Materials to Sliding Wear Using Block-on-Ring Wear Test, 1998.

¹²⁰ J.B. Zu, I.M. Hutchings & G.T. Burstein, *Wear*, 1990, **140** (2), 331.

¹²¹ M.M. Stack & N. Pungwiwat, *Tribology Int'l.*, 2002, **35** (10), 651.

¹²² Morten S. Jellesen, Mads K. Hansen, Lisbeth R. Hilbert & Per Møller, Erosion-Corrosion Behavior of Innovative Hardening Treatments and Coatings on Stainless Steels for Food Industry Applications, *Journal of applied surface finishing*, 2007, **2**, 1, 56-62.

¹²³ M.S. Jellesen, Erosionskorrosion - mekanismer, egenskaber og måling. A conference paper in Danish, presented at DMS Vintermøde and in DMS proceedings: Korrosion - mekanismer, havarier og beskyttelse, ISBN: 87-87535-35-1, pp. 187-204, 2006.

¹²⁴ K. D. Eifird, E.J. Wright, J.A. Bros, T.G. Hailey, Correlation of steel corrosion in pipe flow with jet impingement and rotating cylinder tests, *Corrosion*, 1993, **49** (12), 992–1003.

¹²⁵ H. Dong, P.-Y. Qi, X.Y. Li, R.J. Llewellyn, Improving the erosion–corrosion resistance of AISI 316 austenitic stainless steel by low-temperature plasma surface alloying with N and C, *Materials Science and Engineering*, 2006, **431**, 137–145.

¹²⁶ Y. Iwai, T. Miyajima, T. Honda, T. Matsubara, K. Kanda and S. Hogmark, Evaluation of erosive wear resistance of TiN coatings by a slurry jet impact test, *Wear* 2006, **261**, 1, 112-118.

6. Simulating material degradation

The following section 6.1 describes a case from the food processing industry with high risk of corrosion. Electrochemical investigations of typically used materials are performed in laboratory and compared to metal release found in industry as a part of project MetalinFood. The following sections 6.2 and 6.3 gives background information for the results described in appended papers II-V. In project MetalinFood the production line of canned minced meat was thoroughly described and in the search for new material solutions, possible degradation mechanisms and new materials were investigated in laboratory as given in section 6.2. Optimization of materials exposed to severe conditions was the background for building an erosion-corrosion setup and results from this setup is described in section 6.3.

6.1 Degradation by corrosion

A case with an aggressive food product studied in project Metalinfood is the processing of juice. The following compares metal release values determined at the production site with corrosion studies performed in laboratory. The corrosion properties of stainless steels AISI 304 and AISI 316 in fruit and vegetable juices have been investigated by electrochemical techniques and monitoring of metal release in actual industrial processing. Typical compositions of various juices is given in table 6.1.

Table 6.1 Composition of different juices given for 100 ml.

Medium	Protein (g)	Carbohydrate (g)	Fat (g)	pH	Added NaCl (g)	Viscosity (cSt)
Orange juice	0-1	9	0-1	3.8	0	2.0
Apple juice	0	10	0	3.8	0	1.6
Vegetable juice	0-1	6	0	4.1	0.7	22.8
Tomato juice	1	6	0	4.2	0.5	-

Vegetable and tomato juice are added chloride during production and as indicated in figure 6.1 the combination of chloride and low pH acid increases the risk of pitting corrosion.

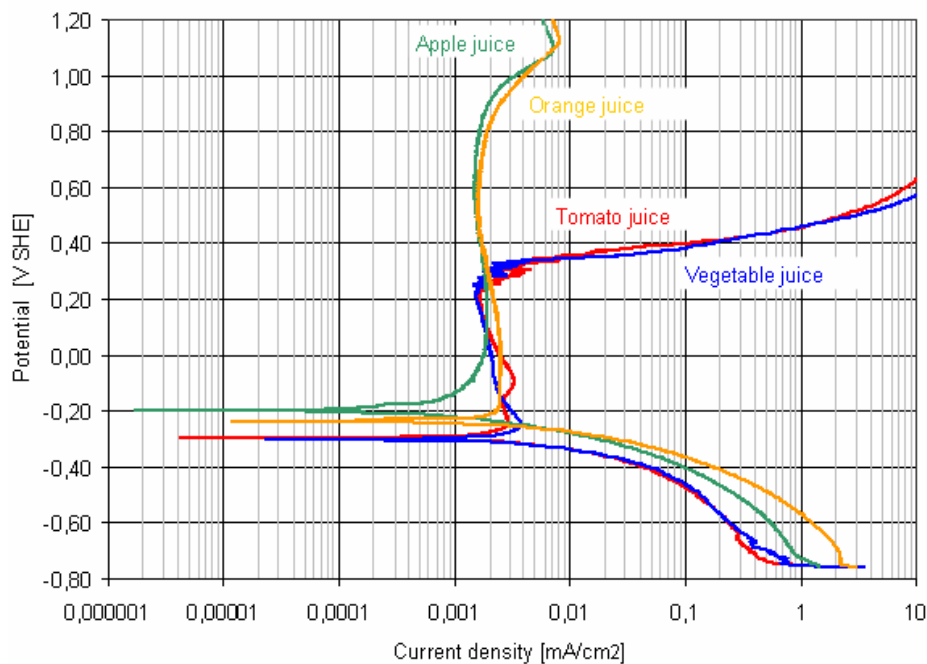


Figure 6.1 Polarization curves for AISI 304 at 30 °C in orange, apple, tomato and vegetable juice at a scan rate of 10 mV/min.

The polarization curves in figure 6.1 show that AISI 304 is passive in orange and apple juice. The current density increases above 1 V SHE due to oxygen development or oxidation of juice ingredients. The curves for the more viscous and chloride containing tomato- and vegetable juices show a lower corrosion potential, but still passivation at a current of 3-4 $\mu\text{A}/\text{cm}^2$. Both the tomato and the vegetable juice degrade the passive film on AISI 304 by pitting at a potential of 0,3 V SHE.

To compare such preliminary laboratory corrosion data with metal release in actual processing of juice during different process step, measurements samples were taken before and after a pasteurizing process and the metal content estimated using Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

Typical process steps in juice production are transportation, cleaning, possibly oils extraction from the peel, juice extraction and pasteurizing. After pasteurizing the juice is typically concentrated by vacuum evaporation at a temperature of around 50 °C. The concentrate is put into cold storage in steel tanks before being transported to suppliers to be diluted and tapped into specific packages. Some juices will be conserved with sulphur dioxide. The presence of sulphur dioxide in fruit pulps has been investigated by Popic et al.¹²⁷ showing that the anodic dissolution of AISI 304 is increasing in presence of sulphur dioxide, because of the oxidative influence of

sulphur dioxide as well as increasing acidity of the electrolyte and interaction of sulphur dioxide with the oxide film.

The pasteurizing occurs at 95 °C for about 20 seconds, whereby micro-organisms are killed and enzymes are inactivated.¹²⁸ Even though this is a short time period for the juice, the pasteurizing tank (typically made of AISI 316) is exposed to this temperature for a longer period. The amount of metal ions in apple juice before and after pasteurizing was analyzed and a notable increase of Fe (given as mg/kg in table 6.2), Cr and Ni was observed.

Table 6.2 Metal content in apple juice before and after pasteurizing as determined by ICP-MS with an uncertainty < 10%.

Specification	Fe (mg/kg)	Cr (µg/kg)	Mn (µg/kg)	Co (µg/kg)	Ni (µg/kg)	Mo (µg/kg)	W (µg/kg)
Before pasteurizing	0.93	8.8	270	7.0	17	5.6	2.0
After pasteurizing	1.5	68	290	7.3	90	6.4	1.8

The concentration of Fe, Ni and Cr increased after the pasteurizing, whereas Mn, Co, Mo and W contents were constant. This indicates that metal increase is due to release from stainless steel and not due to the inevitable standard deviation when determining metal content at such low values. The process equipment did not show any visible signs of corrosion, but these data indicate that pasteurizing is an area of precaution, where intensified inspection and proper cleaning of tanks is essential.

Metal released by corrosion in fruit- and vegetable juices is negligible at ambient temperatures and if process equipment is handled correct. Significant metal release can occur if the electrochemical potential or temperature is raised in tomato or vegetable juice. This can occur either by galvanic contact with a nobler alloy, by external polarisation, e.g. as the juice is conserved with sulphur dioxide, or if deposit corrosion occurs. The details of deposit corrosion have not been studied here, neither has the effect of sulphur oxide being present in juice.

Laboratory tests did not indicate apple juice to be aggressive towards AISI 304 at 30 °C, but metal release data during processing shows an increase of Fe, Ni and Cr released into juice after pasteurizing at 95 °C. Alternative materials to be used at this process step are stainless steel type 316 L or type SMO, since these materials are known to have superior pitting resistance at elevated temperatures. A significant parameter that is not considered in the laboratory testing is the influence of

mechanical stresses due to transport in pipes and in processing steps like homogenizing. The interaction between electrochemical and mechanical influences will be treated in the following.

6.2 Sliding wear in aggressive food products

A case investigated thoroughly in project Metalinfood is the processing of meat into canned minced meat with the risk of metal ions/particles being released into food products. This is an example of a sliding wear contact. By normal procedure the machinery is lubricated by the fat in the meat and ICP-MS data show only minimal increase in metal content before and after the mincing step (table 6.3). If inadequately operated with too high loads, lubrication will be inadequate and excessive tightening of sliding parts may increase wear degradation of sliding parts. Metal release determinations after such an induced initiation are also shown in table 6.3.

Table 6.3 Metal content after the two mincing and fine mixing steps as determined by ICP-MS with an uncertainty < 10%. Results are shown for a normal procedure performed with good manufacturing practise and for an induced initiation with a high load established before the entering meat can lubricate the system.

	Element concentration [$\mu\text{g kg}^{-1}$]						
	Fe	Cr	Mn	Co	Ni	Mo	W
Normal procedure	[mg kg^{-1}]						
Crude mincer	18,6	92	155	2	24	25	29
Fine mincer	10,2	24	97	0,3	11	13	0,4
Fine mixing	9,1	72	146	1	38	37	1,3
Induced initiation							
Crude mincer	43,0	228	325	4	60	42	50
Fine mincer 1	227	1468	1140	20	390	186	7,5
Fine mincer 2*	682	3980	2720	59	1240	577	16,9
Fine mixing	13,8	114	185	3	47	56	6

* Replicates were made to verify the high concentration values.

Comparison of data from normal and induced procedures of minced meat processing, presented in table 6.3, indicate that particles are likely to be released during the induced initiation. For the normal procedure it seems that the metal content remains low. The decrease in values is expressing the inevitable variance with a sampling size of only 2 g. For the induced initiation metal concentrations are higher after the crude mincer and especially after the fine mincer. After the fine mixing step, where the minced meat is mixed with other ingredients, the metal concentrations from the normal procedure and the induced initiation are similar

again, indicating that particles have not been included in this particular ICP-MS investigated sample. Each sample size is only 2 g and more samples or larger sample sizes are needed to follow up the indications of particle release.

Commonly used materials for knives are 80CrV2 or HSS and materials commonly used for the perforated disc is Sverker 21, with the composition given in Table 4.1. Appendix II shows results from these material combinations sliding against each other in a simulant of 0,21 wt.% chloride in aqueous solution. In this work two separate fixed potentials were used for chronoamperometry studing. The open circuit potential during wear is shown in figure 6.2 for each material coupling.

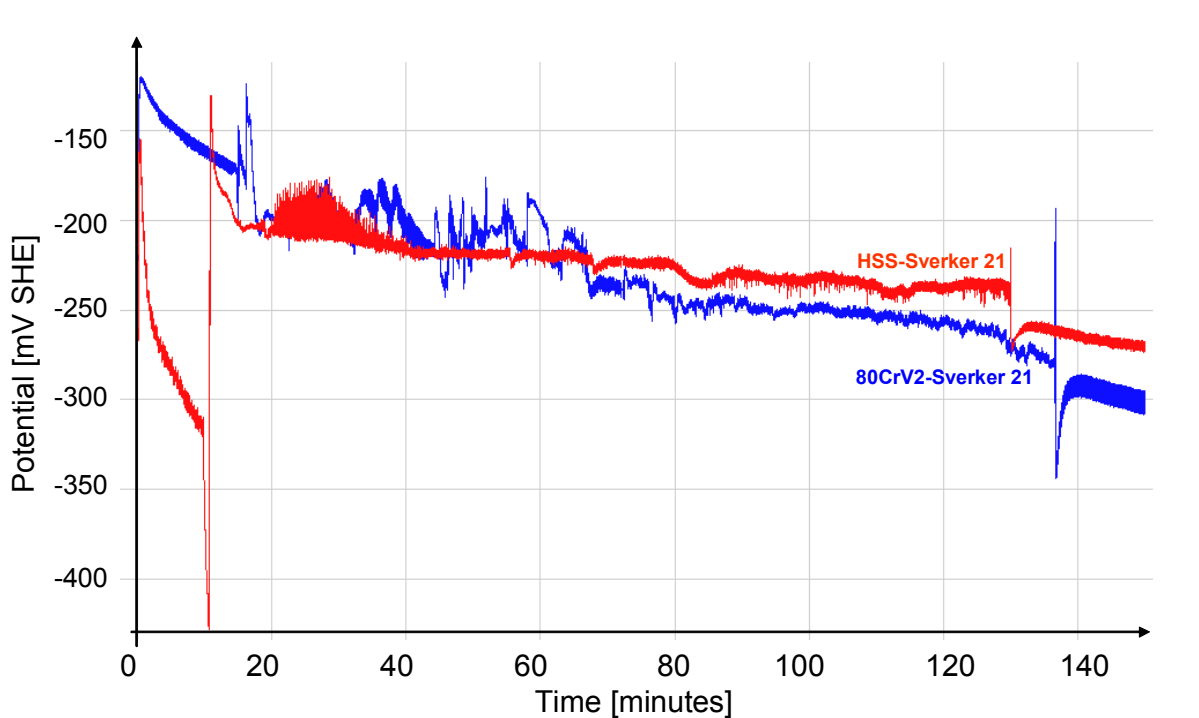


Figure 6.2 Open circuit potential monitoring of HSS block - Sverker 21 ring and 80CrV2 block - Sverker 21 ring couplings in aqueous solution of 0,21 wt.% chloride.

The purpose of this experiment was to evaluate the open circuit potential of the sliding system in order to find a realistic fixed value for chronoamperometry. For the HSS-Sverker 21 combination, coupling took place after 10 minutes and lasted 2 hours. For the 80CrV2-Sveker 21 combination coupling started after 15 minutes. The potential values slightly decrease for both material combinations throughout the 2 hour test period, but ends up being slightly higher for the HSS-Sverker 21 coupling than for the 80CrV2-Sverker 21 coupling.

Tribocorrosion data using the block on ring test setup was also investigated in minced meat (appendix III), but this time using a fixed potential value for all material combinations.

All tribocorrosion tests were again performed at a fixed, increased potential since the processing materials are galvanically coupled to stainless steel in the process equipment. The value chosen for the tests was based on laboratory tests of AISI 316 L in minced meat as reference. The validity of the fixed potential value chosen is not certain and investigations are ongoing to evaluate its exact value in process equipment. The potential value is of great significance, since corrosion accelerates evidently, when increasing the potential for these (relatively non corrosion resistant) materials investigated.



Figure 6.3 A 80CrV2 block after sliding against Vancron 40 ring in minced meat, after removal of the top layer of minced meat.

Materials used for processing meat into minced meat need to be wear resistant, since mechanical interactions like sliding wear contacts with interaction of abrasive particles (possible bone particles or wear debris) are involved. The results in

appendix III indicate that a perforated disc made of Vancron, as an alternative to Sverker, is expected to show a remarkably lower coefficient of friction. Whether or not it will corrode and release significant metal amounts, depends on which electrochemical potential the materials are exposed to during actual processing and cleaning procedures being used. Vancron is now being tested as a process equipment material for mincing meat and is being surveyed by measuring the metal content in minced meat before and after the processing step involving equipment made of Vancron.

A block-on-ring testing facility has been used to evaluate corrosion-, wear- and synergy-parts of metal degradation taking place in minced meat production. Even though a lid ensured that meat will enclose the wear contact at all times, it is not possible to simulate the flow of meat that exists in the actual processing at the meat plant. However, the used block-on-ring tribocorrosion test setup has given insight in corrosion-, wear- and synergy-parts of metal degradation taking place. New process equipment materials have been suggested and are now being tested a full scale in the industry.

6.3 Improvement of erosion-corrosion properties

In order to optimize the surface of stainless steel to withstand erosion-corrosion it is beneficial to determine the material degradation caused by erosion and corrosion respectively, as well as the combined effect. An erosion-corrosion setup as described in section 4 has been used for this purpose. The setup allows specimens to undergo erosion-corrosion while electrochemical measurements are performed. The results can be used to optimize surface properties, estimate life time of process equipment and evaluate effects of environment composition, particle concentration, fluid velocity etc. in food processing systems as well as in other processing systems. Materials known to have improved resistance against erosion-corrosion are titanium, Stellite® and Thyssen Krupp alloys Nicrofer® 5923 and Nicrofer® 3127. Polarization curves of the materials all showed passivation with passive currents all close to $1 \mu\text{A}/\text{cm}^2$ up to 1000 mV SHE. Erosion-corrosion chronoamperometry results are shown in figure 6.4. They show that the current density for titanium evidently increases during erosion, whereas the current densities for Stellite® and Nicrofer® alloys remain low during erosion at this rather high fixed potential of 644 mV SHE. Weight losses were too insignificant to be measured when using a laboratory balance.

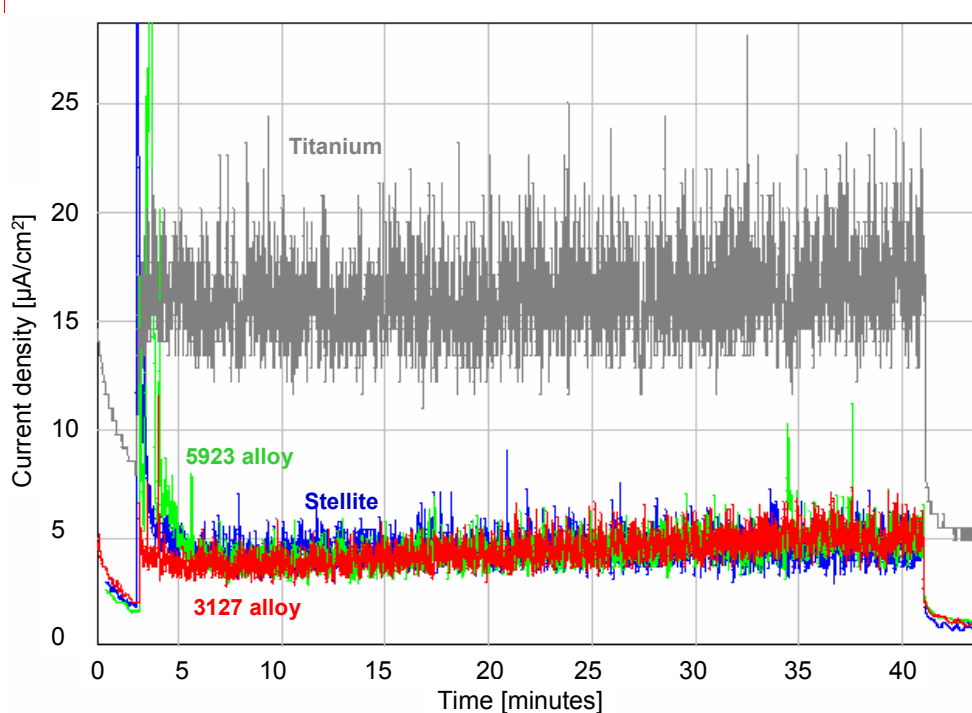


Figure 6.4 Chronoamperometry at 644 mV SHE, eroded with 0,6 g Al_2O_3/l , size 250 μm , 0,5 wt.% NaCl at pH 4 for 38 minutes.

Such highly alloyed metals are expensive and often difficult to machine making them less used than stainless steel. It has been claimed that austenitic stainless steels are particularly vulnerable to erosion–corrosion.¹²⁹ The poor tribological behaviour of austenitic stainless steels has been described as a barrier to their wider application under tribocorrosive conditions¹³⁰ and thus new technologies to enhance the wear resistance of stainless steel surfaces without losing their attractive 'stainless' characteristics are wished for.

Nitrided zones with layer thicknesses from 15 to 30 μm obtained by plasmanitriding are shown in figure 6.5. The hardness of such layers is approximately 1000 HV, but sensitization has occurred at 450 °C meaning that such surfaces are mainly intended for use in non aggressive environments.

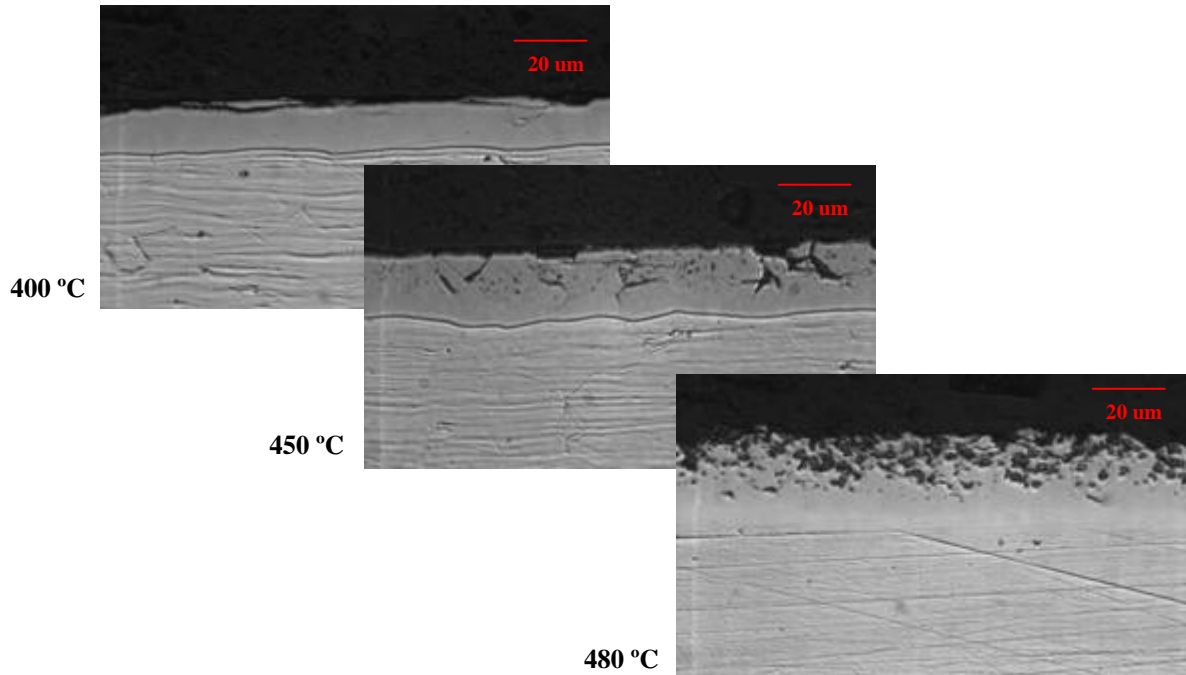


Figure 6.5 Micrographs of plasmanitrided steel at 400 °C for 60 hours, 450 °C for 30 hours and 480 °C for 18 hours, all etched with Kahlings reagent. Precipitation of nitrides has clearly occurred for the 480 °C treatment appearing as black areas.

Chronoamperometry measurements during erosion-corrosion also clearly show that the corrosion resistance is significantly lower for the plasmanitrided samples treated at higher temperature.

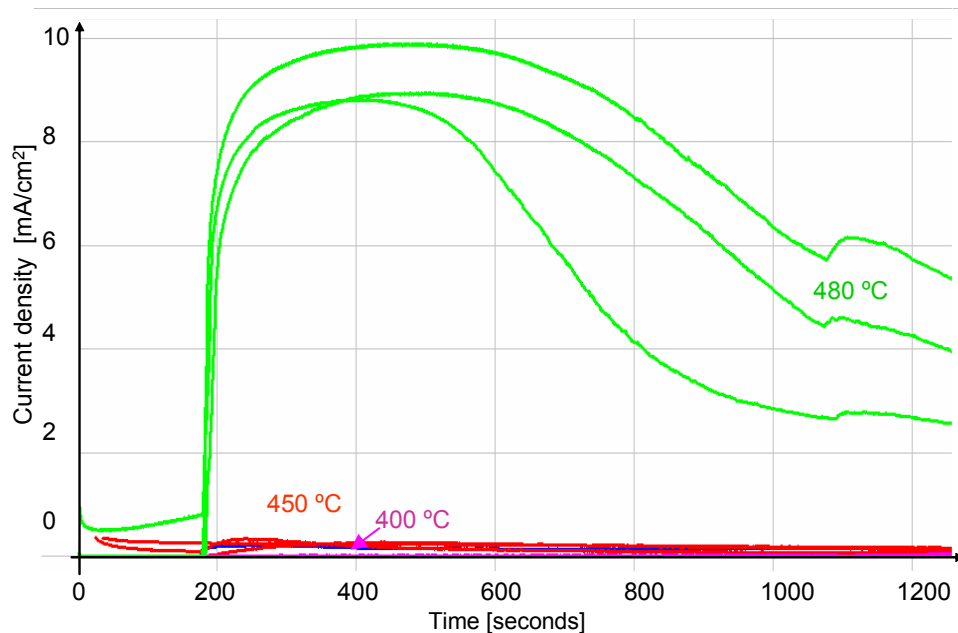


Figure 6.6 Chronoamperometry of plasmanitrided samples (3 repetitions for each temperature) at 644 mV SHE, eroded with 0,6 g $\text{Al}_2\text{O}_3/\text{l}$ size 250 μm , 0,5 wt.% NaCl at pH 4 for 18 minutes.

The erosion-corrosion of low temperature nitrided stainless steel has also been studied with a particle size 105 μm eroded at an angle of 90° with 0,6 g/l Al_2O_3 particles.¹³¹ The solution consisted of 40 l 0,05 M sodium citrate/citric acid buffer at pH 4, with a sodium chloride concentration of 0,5 wt.%. The solution was kept at room temperature and stirring was performed during all experiments. The pump was set to deliver 6,0 l/min and the nozzle had a diameter of 6 mm, resulting in a liquid velocity of 5,2 m/sec. The distance between the specimen and the jet nozzle was fixed at 5 mm. An example of a current monitoring during erosion-corrosion can be seen in figure 6.7 for untreated AISI 316 L and low temperature nitrided AISI 316 L.

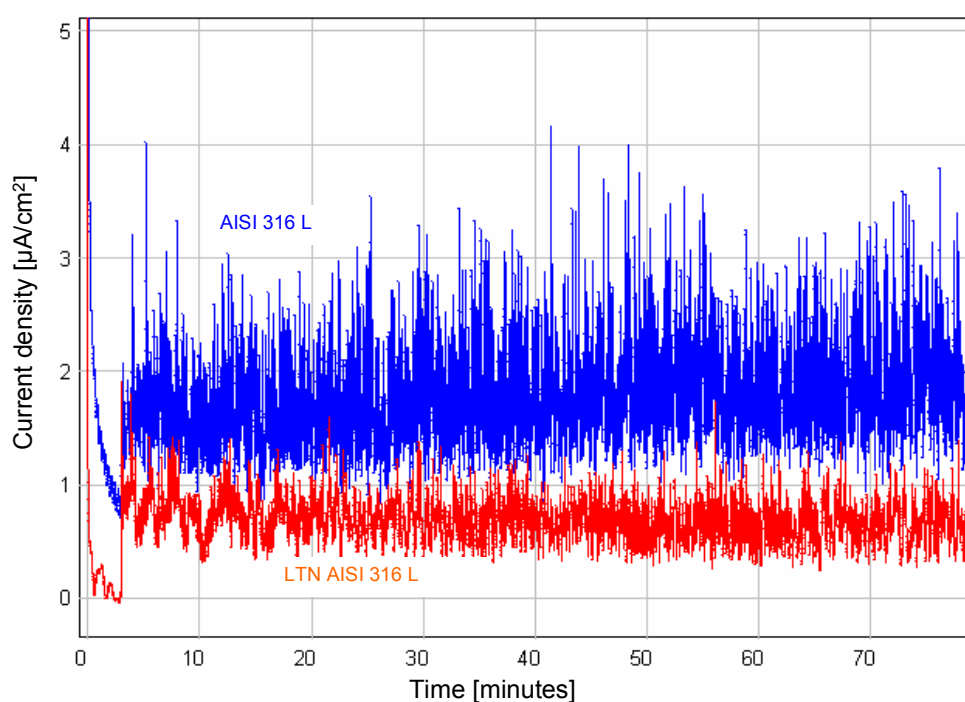


Figure 6.7 Erosion-corrosion of untreated and low temperature nitrided stainless steel at a fixed potential of 644 mV SHE, eroded by 0,6 g/l Al_2O_3 size 250 μm particles in 0,5 wt.% NaCl solution buffered to pH 4.

Again the potential was fixed at 644 mV SHE, which was in the passive region of 316 L in this simulated food product and the current was monitored. The first 3 minutes show that passivation occurs. Then erosion starts and lasts for a 76 minutes test period. The fluctuations are characteristic for each particle impact and less fluctuation indicates larger resistance towards plastic deformation as is the case for LTN AISI 316 L. The average current and total material loss is shown in table 6.4.

Table 6.4 Average current and material losses after erosion corrosion testing.

Specimen	Average current density [$\mu\text{A}/\text{cm}^2$]	Total material loss [mg]
Untreated AISI 316 L	1.8 ± 1	0.01
LTN AISI 316 L	$0.8 \pm 0,5$	Not measurable

Weight loss of the specimens was measured using a microbalance with a sensitivity of 0.01 mg. The result for the untreated sample was just detectable and the material loss for the low temperature nitrided sample was not measurable. It is possible that thorough topographical analysis is the only way to quantify such small material losses. Qualitatively it seems that low temperature nitriding not only decreases the wear rate as compared to untreated stainless steel, but also does so without deteriorating the corrosion properties of stainless steel.

The total material loss should be quantified precisely either by weight loss or topographical measurements to fully understand the mechanism and obtain the exact distinction between erosion, corrosion and synergy parts. Therefore it can be necessary to accelerate the test further and thus 1,9 g/l particles of size 250 μm was used at a distance of 4 mm for a 38 minutes test period in appendix V. When comparing different surface modifications on the same substrate the test setup has been given reliable and useful data for developing wear resistant stainless steel surfaces without losing their corrosion resistance.

Similar experiments have been performed on a conventional PVD duplex treatment used in many wear applications as shown in appendix IV. The PVD duplex treatment hardens stainless steel by plasmanitriding and combines it with a DLC layer on top. This combination supports the top layer and is an appropriate solution in many wear applications. The producers, Tribocenteret at the Technological Institute, Århus, are aware of the treatments poor corrosion resistance and advise their costumers to use this surface modification only in non aggressive environments. Figure 6.8 shows a wear track after erosion-corrosion testing and a SEM micrograph of the corresponding cross section.

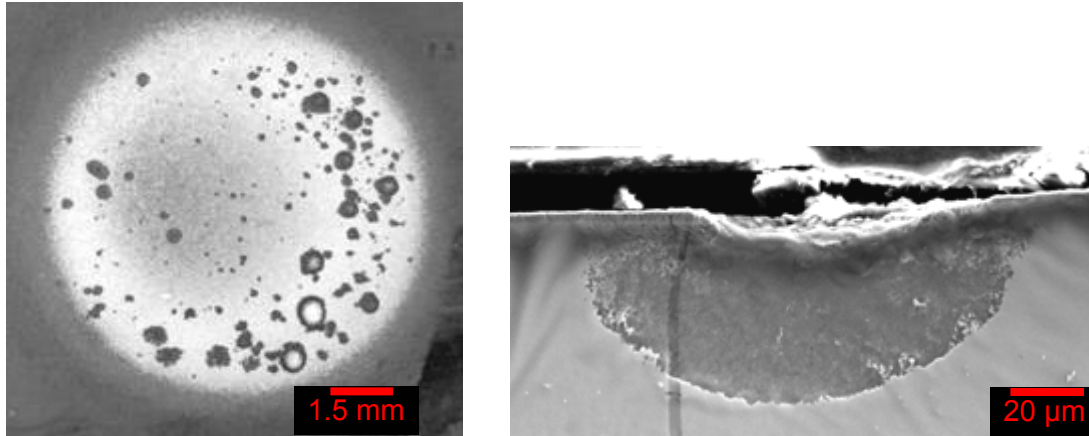


Figure 6.8 Duplex-DLC after erosion-corrosion testing indicating severe local corrosion of the plasmanitrided zone, beneath the DLC layer.

For further investigation of the coatings corrosion properties, electrochemical impedance spectroscopy (EIS) has been performed. The equivalent circuit, shown in figure 6.9 has previously been used as a model for the electrochemical reactions taking place on DLC coated stainless steel.¹³²

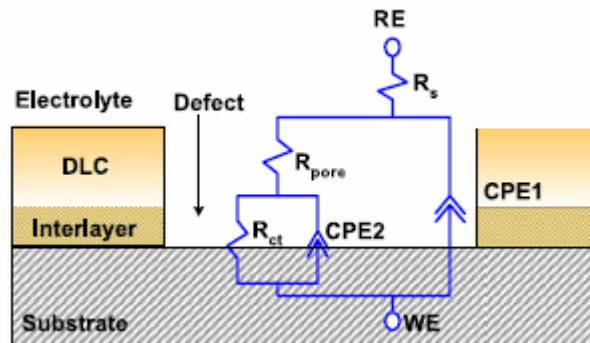


Figure 6.9 Equivalent circuit for investigating DLC and DLC-duplex coatings on stainless steel.¹³²

In figure 6.9 the following denotations are used:

WE is the working electrode and RE the reference electrode.

R_s is the electrolyte resistance between the work and reference electrode.

R_{pore} is the pore resistance in the DLC layer and the adhesion promoting layer.

R_{ct} is the resistance in the interface layer between the DLC layer and the substrate.

CPE1 is the capacitance of the DLC coating including the adhesion promoting layer and pores.

CPE2 is the double layer capacitance of the boundary layer between the DLC layer and substrate.

The electrolyte resistance (R_s) is a function of the media and should be equal for surfaces with the same surface area. The resistance of the solution in pores in the layer (R_{pore}) is dependant of the number of and size of pores. In a defect through the layer the charge transfer resistance depends of the resistance of the boundary layer between the DLC layer and the substrate (R_{ct}). The model does not take into account the specific resistance of the layer without pores, since it expected to have a relatively high value and be of little importance in the parallel connection.

The DLC and adhesion promoting layers also have a capacitance value, which depends of the area of pores. If there is a defect through the layer this capacitance depends on the specific permittivity of the substrate and of the total area of the substrate.

The impedance diagrams of DLC and DLC-duplex coatings fitted with the equivalent circuit can be seen from figure 6.10.

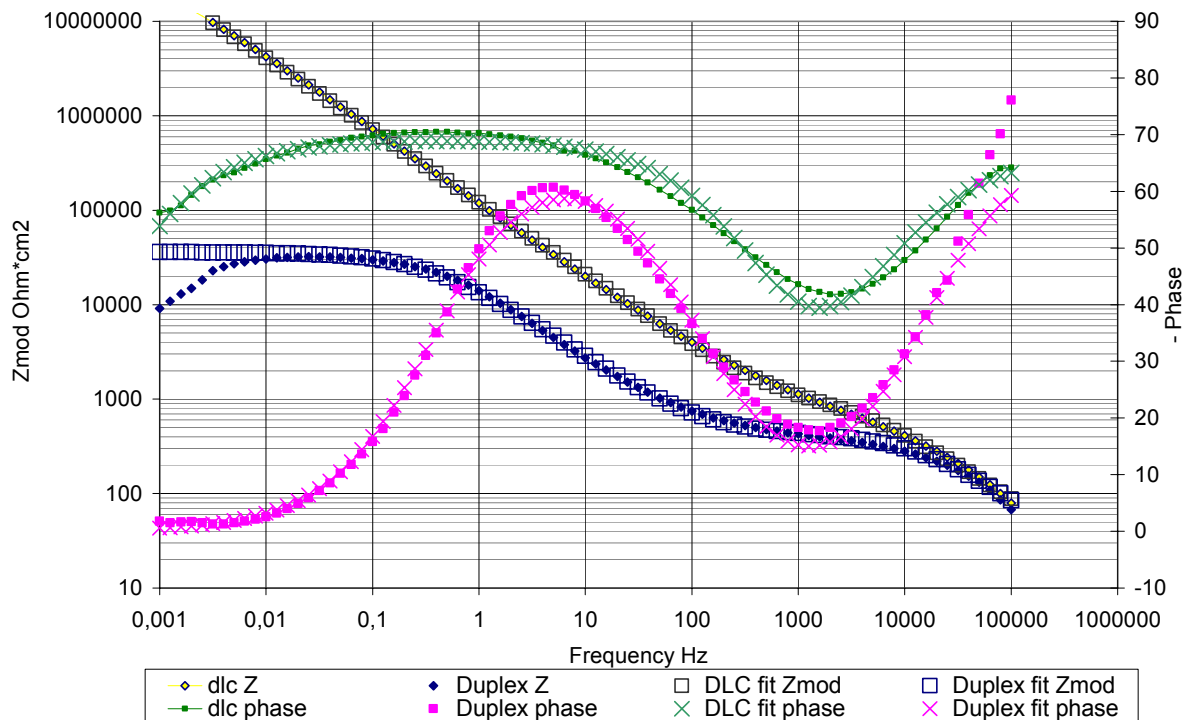


Figure 6.10 EIS Bode plot for DLC and DLC-duplex ranging from 1 mHz to 1 MHz.

The impedance diagrams were interpreted based on the equivalent circuit (Figure 6.9) and the use of a fitting program. The results of the EIS measurements are

presented in table 6.5. The electrolyte resistances are low with values of 1,3 and 3,2 $\Omega\text{-cm}^2$.

Table 6.5 Results of EIS measurements.

Specimen	R_s [$\Omega\text{-cm}^2$]	CPE1 [$\cdot 10^{-6} \text{ F/cm}^2$]	R_{pore} [$\cdot 10^3 \Omega\text{-cm}^2$]	CPE2 [$\cdot 10^{-6} \text{ F/cm}^2$]	R_{ct} [$\cdot 10^3 \Omega\text{-cm}^2$]
DLC	1,3	0,48	1,2	1,53	75.056
DLC-duplex	3,2	0,26	0,4	14,5	36

For the DLC layer the pore resistance is fitted to a value of 1200 $\Omega\text{-cm}^2$ and an very large resistance R_{ct} (75 $\text{M}\Omega\text{-cm}^2$) in the boundary layer between the DLC layer and the substrate can be found. The DLC-duplex layer shows a 3 times lower pore resistance and a 2000 times lower resistance in the boundary layer between the DLC layer and the substrate. The total resistance adds up to be significantly much higher for the DLC coating than for the DLC-duplex coating.

The capacitance values from the two layers are comparable, but the double layer capacitance at the boundary layer is 10 times higher for DLC-duplex than for DLC.

The EIS-measurement indicates that the DLC layer has a higher resistance against corrosion than the DLC-duplex layer. This is primarily due to a higher resistance between the DLC layer and the substrate. DLC-duplex has a slightly lower pore resistance, indicating the presence of more pores in the DLC-duplex layer as compared to DLC. The high double layer capacitance value for DLC-duplex also indicates that a larger substrate area is revealed for DLC-duplex than for the DLC. This means that the electrolyte easier can obtain contact directly to the substrate for DLC-duplex and thus to the conventional plasma nitrided layer which has a considerably lower corrosion resistance than the untreated stainless steel substrate under the DLC coating.

¹²⁷ J.P.Popic, M.L. Avramov-Ivic, I.D. Doroslovacki, *Corros. Sci.*, 2001, **43**, 1601.

¹²⁸ D.K Tressler et al., *Fruit and Vegetable Juice, Processing technology*, The Avi Publishing Company, Inc, Westport Connecticut, 1971.

¹²⁹ P. Shankar, U.K. Mudali, in: H.S. Khatak, B. Raj (Eds.), *Corrosion of Austenitic Stainless Steels*, Woodhead Publishing Ltd., Cambridge, 2002, 340–362.

¹³⁰ Bell T, *Surface engineering of austenitic stainless steel, Surface Engineering*, 2002, **415**.

¹³¹ M.S. Jellesen, L. R. Hilbert and P. Møller, *Corrosion and Wear in the Food Industry*, Conference Paper Nordic Corrosion Congress, NKM 14, Copenhagen, 2007.

¹³² H-G Kim et al., *Thin Solid Films* 2005, **475**, 291-297.

7. Summary of appended papers

This thesis includes a number of appended papers all with the common interest to investigate metal release from materials exposed to corrosion or tribocorrosion.

1. A review of metal release in the food industry

This paper reviews a broad range of published literature on metal release in the food industry. Examples of food products with a corrosive effect are given as apple sauce, pickles, pepper sauce, salted butter and in the field of brewing and distilling. Only a small amount of literature has been published on metal release as a consequence of processing, but some of the few reported failures are summarized in the following table.

Table 7.1 Examples of material degradation in specific food products

Material	Food product	Proces	Failure Type	Metal release
AISI 316	Ketchup	Pumping	Pitting corrosion	Possible Fe, Cr, Ni
AISI 316	Dairy	Pumping	Erosion-corrosion	Possible Fe, Cr, Ni
AISI 316	Citrus	Distillation	Erosion-corrosion	Possible Fe, Cr, Ni
AISI 304	Glucose	Heating	Pitting corrosion	Possible Fe, Cr, Ni
Stainless steel	Miscellaneous	Cooking	-	Ni
Monel	Margarine	Pumping	Erosion-corrosion	Cu, Ni
Chromium alloys	Water	Boiling	-	Cr, Ni
Tinplated steel	Apple sauce	Can storing	Pitting corrosion	Fe, Sn

Examples of degradation of process equipment as a consequence of wear (possibly combined with corrosion) involve processing of margarine, glucose, asparagus and milk powder. A typically mentioned failure type is erosion-corrosion and it was decided to investigate this degradation mechanism further in this work, resulting in papers appended IV and V.

Apart from the reported cases there are most likely numerous cases which are not published and the valuable failure experiences stay between the material supplier and the food processing industry. To support this argument of low information rate on reported failures in the food industry, it can be mentioned that since this paper was published no material failures with resulting metal release into food products has been reported.

II. A block-on-ring tribocorrosion setup for combined electrochemical and friction testing

The block-on-ring test setup was compared with other tribometers by using a model system of a ceramic alumina ring sliding against a stainless steel block in dilute sulphuric acid. The electrochemical and mechanical results were in agreement with results reported elsewhere, but there were fluctuations in the normal force and a dead weight system was developed instead of using pneumatic system. The block-on-ring test setup was also used to investigate equipment in the food industry, where sliding wear occurs. Two material couplings were investigated; Sverker 21 ring sliding against a 80CrV2 block at -286 mV SHE and Sverker 21 ring sliding against a HSS block in aqueous solution with 0,21 wt.% chloride at -216mV SHE.

Table 7.1 Composition of investigated materials.

Material	Fe	Cr	Ni	Mo	Mn	Si	C	V	Co	W
80CrV2	rest	0,5	0,1	-	0,4	0,3	0,8	0,2	-	-
Sverker 21	rest	11,8	-	0,8	0,4	0,3	1,6	0,8	-	-
HSS	rest	4.0	0.3	4.9	0.2	0.4	1.7	1,8	-	6,2

The results showed that HSS is slightly more wear resistant material than 80CrV2. Especially in aqueous solution, the galvanic coupling HSS - Sverker 21, can accelerate corrosion of Sverker 21, due to the higher potential than for a 80CrV2-Sverker 21 coupling. Given that the materials corroded at an accelerated rate in aqueous solution, and since the fat containing meat is likely to influence the wear situation, it was decided to investigate the materials in minced meat as described in appendix III.

III. Corrosion and wear properties of materials used for minced meat production

Combined sliding wear and corrosion conditions in minced meat were simulated using the block-on-ring tribocorrosion setup. The aggressiveness of minced meat was evaluated by potentiodynamic measurements showing that it was less aggressive than a similar chloride containing solution. Therefore chronoamperometric investigations are performed at a higher potential (-156 mV SHE) than in aqueous solution, since the materials perform more noble in the actual food product than in simulating aqueous solution. Vancron was suggested as an alternative material to Sverker and was tested sliding against 80CrV2 and sliding against itself. For Vancron sliding against vancron a remarkably low coefficient of friction was noticed, but also local corrosion was taking place at the elevated potential during chronoamperometric testing.

IV. Erosion-corrosion behavior of innovative hardening treatments and coatings on stainless steels for food industry applications

Materials investigated in the erosion-corrosion test setup were stainless steel type AISI 316 L modified by nitriding and DLC treatments. The environment was a non-specific food simulating solution containing chloride and a low pH. Corrosion experiments were performed in 0,03 wt.% chloride at pH 5,5 and the erosion-corrosion studies in 0,5 wt.% NaCl at pH 4. The erodent was 0,6 g/l alumina particles, size 250 μm at a flow of 6 l/min at a distance of 5 mm from the specimen. Chronoamperometry was performed at a constant potential of 644 mV SHE with a test duration of 2,5 and 10 min.

The results showed that low temperature nitriding decreased the wear rate as compared to untreated stainless steel without deteriorating the corrosion properties of stainless steel. Conventional nitrided layers had inferior corrosion resistance compared to the DLC deposited stainless steel. Initially the properties improved for samples with deposited DLC films, until the thin film broke down and the corrosion rate increased, as compared to untreated stainless steel, by the initiation of local corrosion of the bulk material, propagating similar to the mechanism for crevice corrosion. A DLC coating with a sub-layer of low temperature nitrided stainless steel is expected to resist local corrosion attacks if the top layer breaks down locally. This was investigated in the following.

V. Erosion-corrosion and corrosion properties of DLC coated gas-nitrided austenitic stainless steel

Tests with DLC and gaseous nitriding of stainless steel were performed in the erosion-corrosion test setup. All parameters were set as in the paper described above, but the distance decreased to 4 mm and concentration of alumina particles to 1,9 g/l. This was done to increase the total material loss so that it could be determined by mass balance weighing. The results showed that the anodic current during erosion was smaller for the nitrided samples than for untreated stainless steel suggesting that the corrosion resistance during wear had improved. The investigation of DLC as a top layer on a low temperature nitrided sample showed minimal total material loss compared to untreated stainless steel.

VI. Nickel-containing coins: a health risk for nickel-sensitive individuals?

This paper comments on the inadequate method used in literature to estimate nickel release from coins. Results from chronoamperometry investigations of the euro alloy Cu75 Zn20 Ni5 in the tribocorrosion setup together with atomic absorption spectroscopy results showed that nickel release during rubbing were significantly smaller than without rubbing. This is in agreement with medical results showing no increase in allergic reactions after the introduction of the Euro coin.

VII. Investigation into nickel release rates from coins

The alloys Cu75 Zn20 Ni5 and Cu75 Ni25 as well as a newly stroke euro coin were investigated by dynamic polarization. A euro coin was exposed to tribocorrosion and afterwards examined by SEM and EDS. The Cu75 Zn20 Ni5 alloy was studied by X-ray photoelectron spectroscopy indicating the presence of C and Cl after corrosion. After exposure to tribocorrosion the surface contained a large amount of C together with O, Cu and Zn. A Pourbaix diagram showing thermodynamically stable compounds to be formed of Cu, C O and Cl at various potentials was presented.

VIII. The electrochemical deposition of tin-nickel alloys and the corrosion properties of the coating

The tin-nickel deposited alloy is thought of as a decorative coating to replace nickel in many cases and thereby decrease the risk of allergic contact dermatitis. The alloy has unique corrosion properties and exhibits surface passivation like stainless steel. A number of electrochemical tests, including polarization curves, chronoamperometric studies and tribocorrosion tests were performed to investigate tin/nickel coatings.

Polarization curves illustrated superior corrosion resistance for NiSn when compared to nickel due to the passivity of NiSn alloys. Tribocorrosion results indicated that the resulting current of NiSn was higher at a constant potential of 220 mV SHE as compared to austenitic stainless steel at 100 mV SHE and nickel at 95 mV SHE under the same conditions. In this comparison it was chosen to raise the potential 25 mV above its materials individual open circuit potential giving the impression that NiSn is more susceptible to tribocorrosion. If all materials were tested at same elevated potential (eg. at 220 mV SHE) NiSn might show the lowest resulting current. Therefore comparison between different materials should be performed at same potential rather than at same elevation above individual open circuit potentials.

8. Discussion

Uncontrollable metal release from metallic surfaces in direct contact with food products or skin is undesirable. Toxic metals as mercury, lead, cadmium and arsenic should always be avoided in materials used in applications with possible health risks as a consequence of metal release. In the food industry stainless steel is the most used processing equipment material and the constituents of such alloys can cause allergy or other health related problems, if released in large amounts. Besides possible dermatitis aggravation for severe nickel allergists, there are also hygienic aspects linked to degradation of food industry process equipment caused by corrosion and wear. Also, the financial inconvenience, related to renewing damaged equipment and consumers intolerance with respect to uncontrollable metal additions to food products are disadvantages of metal release.

In cases where both wear and corrosion takes place it is important to select proper materials if there are critical demands for minimizing metal release from the system. This is nondependent whether the material is used as an implant or the material is intended to be used for skin contact or in the fields of pharmaceutical or food production.

The work given in appendices II and III has shown that safe food processing is not always just a question of proper maintenance and replacing worn or corroded parts. More detailed inspection of the degraded parts combined with more complicated test methods can provide important information of the degradation mechanism and thus be a foundation for better materials selection in contact with the material suppliers and process equipment manufactures. Materials used for meat mincing equipment must posses wear resistance, since mechanical interactions like sliding wear contacts and possible interaction of abrasive particles (bone particles or wear debris) are involved. Furthermore the surfaces must also have corrosion resistance. Meat contains chloride and complexing agent such as proteins/polypeptides. In literature the influence of organic compounds as proteins has been observed and described.¹³³ Most often the tonnage of food products is so large that possible ion metal contamination due to tribocorrosion will be diluted to a great extent and thus hard to recover. If metal release occurs as particles it is often difficult to identify them. Larger particles will most often be detected and separated, but small sized particles submicron and non metallic particles may end up in the food product. The exact health risks of such particle contamination are not known and request for new analytic techniques for detecting particles.

The large flow of meat that exists in actual processing at a meat plant has not been possible to simulate using the laboratory block-on-ring test setup. The sliding wear line contact is important to simulate, since it describes the contact geometry in meat cutting equipment (mincers, mixers, microcutters etc.). A significant difference between the production equipment and the test equipment is that the product (the meat) in the test equipment is reused and not replaced by new meat. It is assumed that this difference does not influence the results significantly, because the corrosion media (meat chemistry) does not change much under the experiment. The salt concentration does not change, and proteins are normally very stable when influenced by heat or mechanical interactions. The tribocorrosion experiments carried out directly in the meat therefore gives insight in corrosion-, wear- and the synergetic effects of metal degradation as regards to different material combinations. New process equipment materials have been suggested and a vanadium enriched steel is now being tested a full scale in the meat processing industry.

The investigations with the block on ring tribocorrosion setup were performed in both aqueous simulant solution of chloride (appendix II) and minced meat (appendix III) showing the importance of testing materials in the specific food product, as compared to migration tests in simplified food simulants as given in the European Commission Directive 85/572/EEC. Experiments performed using the erosion-corrosion setup has been performed in aqueous simulants, since the purpose was solely to investigate material properties. If specific food processing cases are to be studied, it is apparent to use the actual food product being processed for testing purposes, since the complex chemistry of food products can affect the degradation mechanisms of materials used for processing equipment in unexpected ways.

The investigation of erosion-corrosion properties showed that massive materials as Stellite[®] and Thyssen Krupp alloys Nicrofer[®] 5923 and Nicrofer[®] 3127 all have impressive resistance against erosion-corrosion. Such massive materials are relatively expensive and can be difficult to machine. Alternatively such materials can be applied by spraying at specific areas exposed to severe conditions. Nevertheless stainless steel is the most well-known material used in the food industry and thus modification of stainless steel for improved resistance against erosion-corrosion has been investigated. DLC coating of stainless steel is one way of improving the materials wear properties without changing the geometry of the part. Investigations of stainless steel with DLC layers directly on top have shown that the layer will flake off during erosion (Appendix IV). In order to improve the mechanical properties of the

bulk material under the layer according to the Hertz theory, nitriding was performed. A conventional PVD duplex treatment based upon plasmanitriding with subsequent DLC coating, used successfully in many dry wear applications, was tested showing that just small cracks in the DLC layer could initiate severe corrosion of the plasmanitrided underlayer. The fixed potential during the chronoamperometry measurement is rather high, which will increase the rate of corrosion as compared to standard situations. However, the result with undercorrosion qualitatively shows the risk of galvanic corrosion between the noble surface layers and less noble bulk materials. In order to improve the corrosion resistance of the nitrided layer, the use of lower temperatures for this process was investigated in plasma as well as simply gaseous nitriding. In order to obtain precise quantification of the total material loss, erosion parameters were made even more severe for the investigation reported in appendix V. These results show that low temperature nitriding is a proper underlayer for thin hard coatings used in tribocorrosive systems, since it apparently can resist local corrosion attacks if the DLC breaks down locally. Cracking of the layer due to impacts can result in initiation of local corrosion of the bulk material, which will propagate similar to the mechanism for crevice corrosion.

When using such severe erosion parameters there is a risk of cracking of thin hard coatings after short test duration due to a high ratio of particle diameter to coating thickness. It has been claimed that impact of very small particles is needed to detach the coating in small fragments in order to evaluate coating properties.¹³⁴ When comparing different surface modifications on the same substrate the test setup has giving reliable and useful data for investigating crack initiation and propagation in thin hard coatings and thus the setup is suitable for development of wear resistant modifications of stainless steel surfaces without loss of corrosion resistance.

Investigations of metal release, not focusing on food/food processing, but in general from surfaces in contact with human skin, have also been carried out. The work given in appendix VI shows how misleading results estimating metal release can be, if inadequate methods are used to estimate nickel release from coins. Results from chronoamperometry investigations of the euro alloy Cu75 Zn20 Ni5 in the tribocorrosion setup together with atomic absorption spectroscopy results showed that nickel release during rubbing was significantly smaller than without rubbing. To further investigate this example of negative synergy between corrosion and wear a Cu75 Zn20 Ni5 alloy was studied by X-ray photoelectron spectroscopy indicating the presence of C together with O, Cu and Zn. A Pourbaix diagram showing

thermodynamically stable compounds to be formed of Cu, C O and Cl was presented and such layers are expected to be formed and smeared on to the surface during handling and thus hindering corrosion.

Also deposited layers as tin-nickel used to replace nickel were investigated under the exposure of mild wear (appendix VIII). In this comparison it was chosen to raise the potential 25 mV above the individual open circuit potential of the material giving the result that NiSn is more susceptible to tribocorrosion than stainless steel and nickel. The evident current increase for NiSn can be due to the top layer of mixed nickel and tin oxide being removed. However, if all materials were tested at same elevated potential NiSn might show the lowest resulting current. Therefore comparison between different materials should be performed at same potential rather than at same elevation above individual open circuit potentials if the objective is to compare materials tribocorrosion properties. If the objective is to estimate metal release from materials, potential values slightly raised over the open circuit potential should be used, to simulate the system more realistically.

The development of test methods, giving the possibility for electrochemically monitoring and controlling materials during exposure to wear, has in all cases shown to provide important information of material degradation mechanisms and material properties.

¹³³ Aleksandra Kocijan, Ingrid Milošev, Boris Pihlar, The influence of complexing agent and proteins on the corrosion of stainless steels and their metal components, *Journal of Materials Science: Materials in Medicine*, 2003, **14**, 1, 69-77.

¹³⁴ Y. Iwai, T. Miyajima, T. Honda, T. Matsubara, K. Kanda, S. Hogmark, Evaluation of erosive wear resistance of TiN coatings by a slurry jet impact test, *Wear* 2006, **261**, 112–118.

9. Conclusion

Tribocorrosion is a significant material degradation mechanism that can cause metal degradation in situations where it is not to be expected. Tribocorrosion can occur in equipment and devices used for critical applications in the food or pharmaceutical industry, in drinking water installations, implants or when surfaces are exposed to skin contact. If inappropriate materials are used in such applications, there is a risk of metal being released as ions due to corrosion or as particles due to wear.

Generally, highly alloyed materials, e.g. Stellite[®], are resistant to tribocorrosive conditions, but the most used material in the food industry, stainless steel, is likely to lose its superior corrosion resistance, when exposed to wear. Nevertheless, tribocorrosion will not always accelerate material degradation. It depends on the material composition and a range of mechanical and chemical factors characterizing the specific tribo-chemical system in which the material is intended to find its use. For example, it has been shown that the metal release from copper nickel alloys decreases during exposure to mild wear, whereas the corrosion rate of stainless steel increases considerably during sliding wear or during erosion with impinging particles. The use of coating technology should also be made with careful consideration of the surrounding system, since coated layers may crack or corrode unexpectedly resulting in detrimental material degradation.

For fast and reproducible evaluation of materials behaviour in regards of tribocorrosion, several test setups have been designed and built in this work. The tribocorrosion testing facilities have their limitations, when compared to exact process conditions and tonnage at full industrial scale, but they give the possibility for testing and comparing various materials and surface modifications under well controlled conditions. The tribocorrosion test setups all give the possibility to monitor/control the electrochemical behaviour of a metal during exposure to wear. This gives a series of information concerning surface properties. It is evident to see, if a metal depassivates during exposure to specific wear parameters, but also the result of galvanic coupling of materials during a wear situation, and possible side effects of wear influencing the electrochemical properties, can be investigated.

A block-on-ring testing facility was used to investigate materials under sliding wear conditions likely to occur for food processing equipment as in e.g. minced meat production. Materials used for processing meat into minced meat must be wear resistant, since mechanical interactions like sliding wear contacts and possible

interaction of abrasive particles (bone particles or wear debris) are involved. The large flow of meat that exists in the actual processing system at a conventional meat plant has not been possible to simulate, but still the results has given insight in corrosion-, wear- and synergy-effects of metal degradation for various material combinations. A vanadium enriched steel has been suggested for as processing equipment and is now being tested a full scale in the meat processing industry.

Investigations with the block-on-ring tribocorrosion setup were performed in both minced meat and aqueous simulant solution of chloride. The investigations show the importance of testing materials in the specific food product as compared to migration tests carried out in simplified food simulants as given in the European Commission Directive 85/572/EEC.

In order to evaluate materials exposed to erosion-corrosion a test setup was built, allowing for monitoring of degradation due to corrosion, during erosion with impinging particles. Comparison of different surface modifications on the same substrate has given reliable and useful data for developing wear and corrosion resistant stainless steel surfaces. Especially the use of diamond-like carbon coatings together with low temperature gaseous nitriding seems promising, since both wear and corrosion properties are significantly improved as compared to untreated stainless steel. Experiments performed using the erosion-corrosion setup has been performed in aqueous simulants, but if specific cases are to be studied it is apparent to use the real food product, since it can provide important information.

External parameters as mild wear can also have an important effect on metal release. This has been proven with the tribocorrosion setup simulating mild wear. During the study of metal release from euro coins an unexpected phenomena was discovered. Normally tribocorrosion has a synergistic effect accelerating material degradation, but in this case an opposite phenomena was observed, since the corrosion rate was reduced. Results from this test setup simulating mild wear can explain the fact observed by medical scientists in skin diseases, that nickel release from the euro-coin (Cu-Ni-Zn alloy) during normal handling is insufficient to elicit allergic reaction in nickel sensitized individuals¹³⁵ and that there has not been any increased in nickel dermatitis after the coin introduction in 2002,¹³⁶ as it was expected from simple migration testing.¹³⁷ Also an electrodeposited intermetallic nickel/tin alloy has been investigated. This alloy has during the last twenty years been recommended for use in skin contact instead of nickel and nickel containing

alloys. Investigation carried out using the tribocorrosion setup simulating mild wear showed that nickel release in sliding contact between skin and metal exceeds the level accepted in EU with the given test parameters. If nickel/tin is tested only by immersion it will pass the EU-test comfortably, in contrast to the Euro-coins, again illustrating the importance of comprehensive testing methods.

Generally, the effects of Ni release from coin alloys and the other investigated nickel containing alloys are considered to be insignificant due to the short handling time of such items. The investigation of such alloys has shown, that tribocorrosion is an unpredictable factor, where the physical and mechanical properties of the corrosion products can play a vital role and how even small variations in the surrounding chemistry can change the corrosion conditions.

The health effects of metal release from food processing equipment are estimated to be negligible, since metals being toxic at low levels are avoided in processing equipment. Possible release of metals as nickel, iron, chromium, molybdenum, tungsten or cobalt will be diluted to a large extent in the large tonnages of food products. Nevertheless, uncontrolled metal contributions to food are not advisable, and hygienic problems may occur on corroded or worn surfaces. Also, the lifetime of equipment can be prolonged if correct materials are implemented instead of continuously replacing parts. More detailed inspection of degraded parts combined with more comprehensive test methods can provide important information of degradation mechanisms and thus be a foundation for better materials selection in contact with the material suppliers and process equipment manufactures.

¹³⁵ Contact Dermatitis, Edited by Frosch, P.J., Menné T., Lepoittevin, J.-P., 4th edition, 2006, ISBN: 3-540-24471-9.

¹³⁶ Zhai H., Chew A.L., Bashir S.J., Reagan K.E., Hostynek J.J., Maibach H.I. Provocative use test of nickel coins in nickel-sensitized subjects and controls, *British Journal of Dermatology*, 2003, **149**, 311-317.

¹³⁷ Nestle F.O., Speidel H., Speidel M.O, *Nature; Metallurgy*, 2002, **12**, 132.

10. Outlook

Although there is only limited literature published on material degradation in the food industry, there seems to be quite an interest in new materials with enhanced corrosion and wear properties. Since all materials must be thoroughly tested before being implemented in process equipment, it is important to have the possibility for fast and reliable screen tests in the laboratory. Such laboratory techniques simulating mechanisms as e.g. tribocorrosion can with great benefit be standardized for a range of food processing industries. Standardized testing, allowing for detailed studying of material degradation, would be a great help for materials selection in many branches of the food industry.

Food processing equipment parts exposed to corrosion and wear might benefit from surface modification rather than changing base material. The hardening of stainless steel with sufficient depth and carrying capacity without deteriorating the corrosion resistance is an area with high industrial potential, and detailed testing setups and techniques giving fast and reliable results are necessary for the development of this innovative area. This work has studied diamond-like-carbon coatings on top of various nitriding treatments of stainless steel under erosion-corrosion conditions. It is apparent future work to investigate such multilayer coatings under sliding wear conditions where the lubricating properties of such coatings are likely to be beneficial. Investigating such multilayers in the block-on-ring tribocorrosion setup will make it possible to compare theory for Hertz pressure with laboratory results for various hardening depths and with elaborating information from the corrosion monitoring.

In the study of meat mincing process equipment the question arose whether metal is being released as ions or as particles so small, that they will not be detected. The exact health risks of such small particles are not yet established and quantification of particles in food products ask for new analytic techniques for detecting particles. Experiments in project MetalinFood using enzymatic techniques where lipids, proteins and RNA are cleaved in small organic molecules resulting in a low viscous solution have shown to be promising for separating metal particles for further investigations by centrifuging.

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Appendix:

Appendix I:

A review of metal release in the food industry

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A review of metal release in the food industry

M. S. Jellesen, A. A. Rasmussen and L. R. Hilbert*

The objective of this review is to outline literature on metal release in the food industry. Key results are reviewed from publications with high scientific level as well as papers with focus on industrial aspects. Examples of food products with a corrosive effect are given, and cases concerning processes, storing equipment as well as cleaning and sanitising procedures are reviewed. Stainless

steel is the most widely used metallic material in the food industry; however other metals and their alloys are also briefly treated. The review deals with phenomena mainly relating to electrochemical corrosion, but also examples of material degradation as a consequence of wear and corrosive wear are presented.

1 Introduction

Metal degradation is a major concern in the food industry. A corrosive environment, wear and the combination of corrosion and wear can cause degradation of equipment and thereby financial inconvenience relating to the renewal or repair of damaged equipment. Additionally, material degradation resulting in metal release can eventually cause health risks for consumers.

Stainless steel is a widely used material in the food industry and is generally resistant to corrosion. Corrosion can nevertheless become a problem when stainless steel is exposed to corrosive food products or to chlorine, commonly used to sanitize equipment. The total estimated stainless steel cost for the food-processing industry in the U.S. is \$1.8 billion per year. This cost includes stainless steel utilized in beverage production, food machinery, cutlery and utensils, commercial and restaurant equipment, and appliances [1]. Metal degradation can cause metal release in form of ions, wear particles or of larger parts causing immediate process shutdown or failure. This review focuses on continuous metal release and enumerates papers from a broad variety of journals and recapitulates the area of metal release reported in the food industry.

2 Allergy to metal in food

Systemic contact dermatitis caused by metal in food has been reviewed in 1997 [2]. The review reports investigations concerning aggravation of dermatitis among nickel-sensitive women, hand eczema improvement after low-nickel dieting and aggravation of dermatitis after ingestion of chromate and cobalt. It has been estimated that the prevalence of nickel allergy in the Danish population is about 10% for women and 3% for men [3, 4], among those around 10% percent are sensitive to nickel contained in food [5, 6]. It has been demon-

strated that oral nickel exposure elicits skin reactions in nickel sensitive individuals [7], but nickel in food cannot always be considered as a source of health risks. Investigations even suggest that oral intake of small amounts of nickel apparently can prevent the development of nickel allergy [8]. According to the Council of Europe nickel intake via food does not cause hazards for the majority of consumers, however the council acknowledges investigations showing a flare-up of eczema through ingestion of even small amounts of orally ingested nickel [9].

Nickel observed in food can arise from many distinct sources [10]. Products such as chocolate and coffee have been observed to have a high natural content of nickel, whereas products such as tomatoes have been observed to have a very low natural content of nickel. Apart from the natural content, the possibility of nickel arising from the production or storage of food should also be considered. Product quality, health, and sanitation issues are major concerns in the food industry. The industry cannot tolerate corrosion deposits in the manufactured product and neither will the customers accept metal enrichment in food during processing.

In 1985 and 1986 *Smart* and *Sherlock* published the papers "Chromium in foods and diets" and "Nickel in foods and diets", respectively, covering general aspects of the fields [11, 12]. They conclude that food is the main source of chromium and nickel intake by man, as compared to air and water. They also state that it is primarily the use of nickel in utensils, food-processing equipment and in catalysts, which can lead to the contamination of food by nickel. The papers show experimental results of chromium and nickel determination in various food groups. Chromium was observed to be fairly evenly distributed throughout the various food groups examined. The highest concentrations of chromium were found in shellfish, meat, fish, fruit, and sugar groups. The highest concentrations of nickel were found in canned vegetables, sugars, bread and cereal food groups, suggesting a contribution from food processing equipment and possible canning.

3 Metallic materials applied in the food industry

Metals and alloys are used as food contact materials in industrial processing equipment, involving handling of the product from harvest until the product reaches the consumer. Food contact metals and alloys are regulated by The Framework Regulation (EC) 1935/2004 [13] which states that food

* L. R. Hilbert, M. S. Jellesen

Department of Manufacturing Engineering and Management, Technical University of Denmark, Kemitovet, DTU Building 204, Dk-2800 Kgs. Lyngby (Denmark), E-mail: lrh@ipl.dtu.dk

A. A. Rasmussen

IPU, Institute for Product Development, Produktionstorvet DTU – Building 424, Dk-2800 Kgs. Lyngby (Denmark)

contact materials shall be safe. It is stated that contact materials shall not transfer components into the food in quantities that could endanger human health, change the composition of the food in an unacceptable way or deteriorate the taste and odour of foodstuffs. Guidelines concerning materials intended to come in contact with foodstuffs are given in a more technical document made by the Council of Europe's Policy Statements [9].

In the food industry stainless steel is most widely used and is therefore thoroughly reviewed in section 3.1. Literature concerning other metals and their alloys are more briefly treated in section 3.2.

3.1. Steel and stainless steel

Steel and especially stainless steel is regarded the most utilised metallic material applied in the food industry [14, 15], particularly stainless steel types AISI 304 and AISI 316. The number of stainless steels available for the fabrication of food processing plants has increased substantially in the past decades. Duplex stainless steel (ferritic and austenitic) and "super-austenitic" stainless steel are given as examples of steels with larger corrosion resistance than AISI 304 and AISI 316 [15]. A few authors have suggested using nickel free stainless steel in order to avoid nickel release into food products [16, 17]; however in many cases such types of steel do not fulfill the requirements of other relevant properties such as mechanical properties and corrosion resistance.

Corrosion problems of stainless steel in the food industry can be attributed to the inappropriate selection of steel for particular applications, incorrect fabrication or design, and incorrect cleaning procedures [15, 18, 19]. Stainless steels commonly fail by localised corrosion mechanisms, arising from transient environmental conditions. Main factors affecting the performance of stainless steels in the food industry are summarised by *Betts, Wells and Lichti* in [15]. *Betts, Wells and Lichti* states that chloride concentration and temperature are regarded as the most common factors implicated in failure, but that the corrosion performance also strongly depends on buffer capacity of the solution. The stability of localised corrosion processes is dependent on the development of a localised, low pH environment next to the metal. Stainless steel in contact with an unbuffered low chloride-containing solution is often more susceptible to localised corrosion than when exposed to buffered high-chloride solutions. An example of local corrosion is given in Fig. 1 where ketchup, with a pH of 3.5, a sodium chloride content of 3.8% and a temperature of 90 °C has caused severe pitting attack to a pump casing made of AISI 316.

Wrong use of cleaning and sanitising chemicals has also been observed to cause failure of stainless steel. Examples of this are given separately in section 5.3. Some organic fatty acids are well-known corrodents of non-molybdenum containing stainless steels causing general surface attack. These include acetic, citric, lactic and tartaric acids, which can lead to general corrosion at temperatures above 70–80 °C.

Finally inadequate design/fabrication procedures may cause failures. Examples are reduced corrosion resistance as a consequence of incorrect welding or heat treatment of stainless steel, tight pipeline radials bends, stagnant ponded areas, and unnecessary crevices and gaps [15, 18]. A compendium by *Page* gives a summation of causes of failures of stainless steel investigated by a large chemical company in the U.S as shown in Fig. 2.

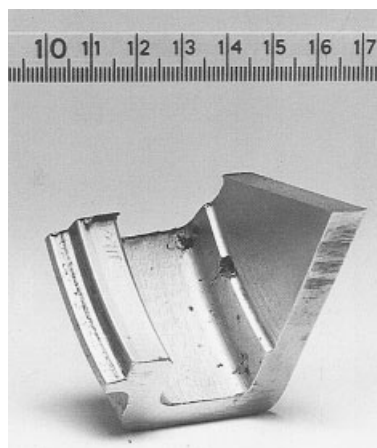


Fig. 1. Part of a cast pump casing (AISI 316) used in a ketchup plant. Pitting corrosion due to high chloride content has caused failure in 6 months [19]

The above cited literature concerning corrosion of steel and stainless steel has centered on general corrosion aspects, without focusing on how these corrosion problems may affect the nickel and chromium content of the food. *Kuligowski and Helpern* [21] have however observed stainless steel to be a significant source of nickel, chromium and iron in food from home and commercial cookware, and the authors recommend that nickel-sensitive patients change to materials other than stainless steel.

Bell has published a paper discussing the poor tribological behavior of austenitic stainless steel [22], which has been a barrier to wider application. *Bell* also discusses the various possibilities of improving the wear resistance and hardness of the austenitic steels without reducing the corrosion resistance and recommends low temperature nitriding and caburising techniques. A severe wear situation for stainless steel is known to be galling, but even negligible wear can cause increased material degradation in corrosive environments. Materials for processing in the food industry are expected to be especially vulnerable to combined corrosion and wear, given the lubricant limitations. An example of combined wear and corrosion has been detected in a distillation column made of AISI 316 for a plant processing natural pectins extracted from

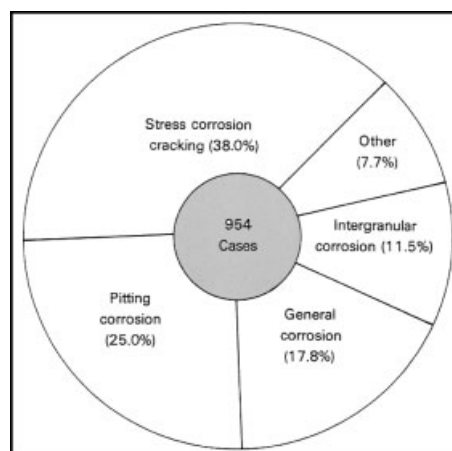


Fig. 2. Summation of causes of failures of stainless steel investigated by a large chemical company in the U.S. [20]

citrus [23]. Material degradation was observed subsequently to a modification of the original plant layout causing an increase of operating temperatures and turbulence of the process stream inside the column. It is suspected that the continuous removal of the protective film at the surface of the plates, exposing new reactive surfaces, caused the extended erosion-corrosion phenomenon observed.

3.2. Metals other than steel and stainless steel

3.2.1 Nickel and nickel alloys

Metal release from pure nickel and nickel alloys should obviously be avoided in order to minimize the nickel content in food, and most often such materials are avoided in the food industry. Monel is a nickel-copper alloy originally thought of as a corrosion resistant material, but under the influence of combined corrosion and erosion the Monel alloy is severely attacked as shown in Fig. 3. In [19] it is suggested to replace the valve regularly as a remedy. From a food safety point of view this solution is undesirable and a more sustainable solution is needed.

An alloy such as amorphous Ni-P may, however, show remarkably good corrosion and wear properties, when used under right conditions and is sometimes considered as a usable material in the food industry according to [24]. In 1999 a study of the release of nickel to water from electric kettles showed that 10 out of 26 kettles released more than 50 µg/l. Seven of these kettles were having nickel-plated heating elements [25].

3.2.2 Chromium and chromium alloys

Pure chromium and chromium alloys are used in the industry as surface layers on other materials for the improvement of for example hardness properties. Apparently these materials are rarely used as contact material in the food industry. In the study of electric kettles, nickel release to water were found to exceed 50 µg/l for two chromium plated copper heating elements, due to migration from an underplate of nickel [25].



Fig. 3. Back-pressure control valve (Monel) of the mixing chamber of the pump of a margarine cooler. An unused specimen is shown to the left and a severely attacked specimen to the right. Erosion-corrosion is caused by the salt-containing margarine combined with high local velocity [19]

3.2.3 Titanium and titanium alloys

Titanium exhibits very high resistance to corrosion, low specific weight, very low toxicity and high biocompatibility [26, 27]. The current reduction of the price of titanium suggests that it might be an attractive material to be used in some food industry applications. These considerations have inspired Feliciani et al. [26] to evaluate the hygienic-sanitary safety of titanium in contact with some aggressive food simulants, and they find that titanium could be regarded as an alternative to stainless steel in the food industry.

3.2.4 Aluminium alloys

Aluminium forms a protective passive layer in relatively neutral environments, and therefore often provides high corrosion resistance in such environments. However, aluminium often tends to corrode when subjected to acidic food or cleaning and sanitising agents. Strong salted food product can also promote corrosion of aluminium. The Danish guideline on materials in contact with food, recommends not to boil water for preparation of baby food in aluminium utensils, since aluminium in too high amounts, can be regarded as a health risk for babies [28].

3.2.5 Lead, cadmium, mercury, tin, and their alloys

Limit values of the content of lead, cadmium, mercury and tin in food are given by [28–30]. Cadmium and mercury as metals are normally not used as contact materials to food. Lead is sometimes used (together with tin) as a soldering material, and investigations have indicated possible release of lead to food from solders [31]. Tin is used as a surface layer on steel in cans for food storing, which is more extensively described in section 5.2.

4 Metal release observed in specific food products

Literature with examples of material degradation in specific food products are treated in this section. Food products often have low pH values or contain corrosive ingredients as salt and thereby extend the risk for failure by local corrosion. [32] The following reported environments are not comprehensive of all corrosive food products, but only of the ones reported in detail. Processing, viscosity, temperature and humidity are also factors investigated concerning metal release to the food product.

4.1 Apples

In 1975 Page et al. [33] reported corrosion problems with canned apple sauce. Apple sauce has a low pH and is normally successfully canned at low temperatures. In the present example the apple sauce was canned in tinplated steel cans. Lids of test packs were observed to suffer from pitting corrosion and the apple sauce suffered from purple colouration. Pitting was only observed in areas where voids were in contact with the lid, since condensation occurred in the void space and in this area the iron corroded. In the areas where the apple sauce was in direct contact with the lid, the tin corroded which gave cathodic protection to the underlying steel. The corrosion problems

were directly associated with the viscosity of the apple sauce, since voids could more easily be removed from the lit, by inverting the can, when the apple sauce had a low viscosity [32, 33].

On the background of studies showing a possibility of a significant rise in haemoglobin values in humans from the intake of food exposed to iron cookware *Rosanof* and *Kennedy* investigated the bioavailability of iron produced by the corrosion of low-carbon steel (99%) in contact with Red Delicious apples [34]. A high percentage of the ingested iron was converted into haemoglobin iron, and ingestion of one Red Delicious apple that had been exposed to eight large iron nails for 24 h could provide 10–15 mg having good bioavailability.

4.2 Pickles, peppers and pepper sauce

A few authors have published literature concerning the production of pickles, peppers and pepper sauce [35, 36]. These products contain corrosive ingredients such as salt and vinegar, and the processing and storage plants often operate under high temperature and humidity. The authors describe in general terms, how the production plants can be improved in order to avoid corrosion by choosing appropriate materials and surface treatments, however no detailed description is given on how the problems concerning corrosion can be solved.

4.3 Asparagus

In a paper from 1997 *Amaro-López* et al. [37] investigated the variation of chromium and nickel content during industrial processing of white asparagus. They reported that the nickel and chromium content of the asparagus varied during certain industrial processing operations such as washing, peeling and blanching, depending on the portions, the diameters of the asparagus, and the varieties (Desto and Sur). The authors did not give explanations of the observed variations of the nickel and chromium content.

A paper from 1997 investigates the influence of frozen storage on chromium and nickel contents in white asparagus [38]. The mean concentrations observed were 0.61 ± 0.18 and 4.23 ± 0.56 mg/kg (dry weight) for chromium and nickel, respectively. Significant differences during frozen storage for both chromium and nickel were observed. The authors did not discuss the origin of the nickel and chromium content.

4.4 Dairy products

Packing of salted butter in metal cans has been discussed by *Page* et al. [39] in 1983. Salted butter is potentially corrosive to metal containers. However, the authors conclude that adequate protection can be achieved in lacquered cans, if proper control of several listed factors is assured. These factors include the control of the butter, the can, the filling and the storage conditions.

Moreno-Rojas et al. published results in 1999 showing variations in lead and cadmium contents during pasteurising, sterilising and desiccation to obtain powdered milk [31]. It was indicated that lead possibly was released from solders. The case history of a pump impeller made of AISI 316 used for milk powder manufacturing is shown in Fig. 4. The impeller was used for processing skimmed milk at 70 °C. Cavitation



Fig. 4. Pump impeller (AISI 316) from a vacuum evaporation system for milk powder manufacture. Material is worn away locally after 1 year of use [19]

has occurred due to steam bubble formation and implosion at the exit side of the propeller.

Sánchez et al. have published a paper showing variations in nickel content during the process of making and ripening Manchego-type cheese. It was indicated that nickel possibly was released from metals during processing [40].

4.5 Wine, brewing and distilling

Baalen discusses the use of stainless steel in wine tanks and concludes that it is an ideal material for the construction of wine tanks [41]. *Cowan* has published a paper concerning corrosion prevention in stainless steel used in brewery process equipment [42]. Commonly encountered corrodents in this field are listed in Table 1.

The list is by no means exhaustive, but represents major areas where corrosion problems have been experienced with stainless steel equipment in the field of brewing and distilling [42].

Table 1. Potential corrodents which are commonly encountered in the field of brewing and distilling [42]

Service liquids	Water supplies
Cleaning agents	Refrigerant brines Sodium hydroxide solution (at certain concentrations and temperatures) Mineral acids Sulphamic acid
Sterilising agents	Sodium hypochlorite Halogen release agents Iodophors
Products	Brewing liquor Liquid sugar (Fruit juices and wines preserved with sulphur dioxide) (Fruit juices containing added salt)

4.6 Glucose

Page has published examples of four instances of premature failure of AISI 304 [43]. One instance occurred because of wrong cleaning procedures causing pitting corrosion. In the other three examples the manufacturer had provided heating for bulk storage syrup. AISI 304 suffered from premature pitting and cracking. This has been explained by the fact that small quantities of hydrochloric acid were added to the product. Together with the original chloride content of the corn and the heating, corrosion was initiated, for example in areas where the chloride was permitted to concentrate because of evaporation at the surface of the stainless steel.

An investigation concerning shaft-supporting bushings in a sugar worm conveyor has also been reported. The tribological behaviour of food grade polymers against stainless steel in dry sliding wear and with sugar was investigated [44].

The reported failures in section 3 and 4 are summarised in Table 2. Failures are mainly reported in food products having low pH or food products containing corrosive ingredients as salt and thereby extending the risk for failure by local corrosion. Also combined corrosion and wear have resulted in unexpected failure of equipment. The given examples of material degradation in specific food products are not a comprehensive report of all corrosive food products, but only of the ones reported in detail. The food industry can be considered conservative in material selection and are often cautious when reporting failures because of consumers' alertness and demands for food safety and quality. Literature concerning metal release observed in processes used in the food industry is described in the following section.

5 Metal release observed in processes used in the food industry

Board has published a paper covering general aspects of corrosion control in the food industry in the early 1970's [13]. As today the process equipment in contact with food was mainly constructed in stainless steel. Even though much information on corrosion resistance was available at the time, the author found that unsatisfactory types of steel were sometimes used for particular applications. Faulty design or faulty fabrication and incorrect cleaning procedures are given as other examples having caused corrosion of stainless steel equipment in the food industry. *Board* states that the most extensive development on corrosion control in food-processing equipment at that time dealt with tinsplate and aluminium cans. Internally lacquered cans for highly corrosive products also received a lot of attention in that period. Selected processes used in the food industry and the use of home cookware are discussed individually below.

5.1 Home cookware

In a paper from 1997 *Park et al.* [45] have studied iron content increase in food due to the use of stainless steel cookware. They conclude that cooking food in stainless steel utensils significantly increases the iron content. The paper does not contain results of measurements of nickel and chromium, and the type of stainless steel used in the experiment is not given; only the types of the used cookware and the names of the company fabricating the cookware are given.

As earlier mentioned *Berg et al.* [26, 46] have investigated release of nickel and other trace elements from electric kettles and coffee machines sold in the Danish market. Many of the kettles included in the investigations released more than 50 µg/l nickel to water. These results lead to a change of construction or design of the kettles in order to ensure a degree of nickel release lower than 50 µg/l nickel. A few kettles were withdrawn from the market. The coffee machines tested did not release trace metals in quantities of any significance.

Flint and Packirisamy [47, 48] have investigated nickel and chromium release from stainless steel cooking utilities, and found that apart from aberrant values associated with new pans on first use, the release of metals to the diet is negligible. The amount of nickel derived from the utensils in standard portions of various "aggressive" foodstuffs tested was found to be 0–8 µg/portion. *Christensen and Möller* have investigated the nickel release from boiling water in stainless steel saucepans. The investigations showed that nickel release could be correlated to the acidity of the boiling water and therefore they advice patients with nickel allergy to avoid stainless steel cooking utensils since lingonberries, rhubarb and apples may provide an acidic environment during processing [49].

5.2 Cans for food storing

Much literature is published on metal release from cans for food storing [50–63] describing stress corrosion cracking in plain tinsplate food cans, product discoloration, filiform corrosion, pitting/perforation corrosion and loss of adhesion in enamelled food cans. For instance intergranular stress corrosion cracking of uncoated tin plates occurred in canned pineapple juice. Black discolouration of rice granulates in the can headspace of a chicken and rice product was caused by the formation of metal sulphides. The blackening of white tan-coloured olives and brine occurred after 1 year of storage in enamelled tinsplate containers as a result of pitting corrosion [64].

In a paper from 1989 *Kamm* [56] discusses the progress in materials for can stock. He summarises that tin-free and low tin materials are being used in drawn and welded cans, but

Table 2. Examples of material degradation in specific food products

Material	Food product	Process	Failure Type	Metal release
AISI 316	Ketchup	Pumping	Pitting corrosion	Possible Fe, Cr, Ni
AISI 316	Dairy	Pumping	Erosion-corrosion	Possible Fe, Cr, Ni
AISI 316	Citrus	Distillation	Erosion-corrosion	Possible Fe, Cr, Ni
AISI 304	Glucose	Heating	Pitting corrosion	Possible Fe, Cr, Ni
Stainless steel	Miscellaneous	Cooking	-	Ni
Monel	Margarine	Pumping	Erosion-corrosion	Cu, Ni
Chromium alloys	Water	Boiling	-	Cr, Ni
Tinsplated steel	Apple sauce	Can storing	Pitting corrosion	Fe, Sn

better enamel coverage is required than for tinsplate cans. Long term trends show that aluminium has taken over most of the beer and soft drink market, but its use in food cans remains very limited. At that time new processable multilayer plastic barrier materials were introduced as cans, bowls and trays for single serving microwave foods, which were expected to have a significant impact on metal cans. In 1989 *Palackdharry* presented a so-called "interior two-coat system for metal food closure" to be used on baby food containers [65]. The coating was presented as being significantly improved according to flexibility and hardness, as compared to commercial three-coat systems of the time.

Concerning storage in larger scale *Cleland* in 1994 published a paper on corrosion in crop storage silos [66]. Corrosion of galvanised steel sheet exposed to a normally benign substance, oilseed rape, was observed to occur at an unacceptable level due primarily to moisture ingress, which was itself due to deficiencies in design, materials and construction. The consequent degradation of oilseed rape produced a complex mixture of chemicals, among other things formic and acetic acids, which were very aggressive towards galvanised coatings and steel.

5.3 Cleaning and sanitising procedures

Cleaning and sanitising chemicals are commonly used in the food industry to maintain strict plant hygiene requirements. Wrong use of such chemicals has often been observed to cause failure of stainless steels [67, 68]. According to *Betts* et al. the probability of failure of stainless steel caused by such chemicals is largely determined by the concentration of oxidants in the solution. It is often the interaction of oxidants with food process streams that result in corrosion damage, not necessarily the corrosivity of the oxidants themselves [68]. Two main classes of sanitising chemicals have been identified by [69]; halogen-based and surfactants. A third class, which is basically strong oxidising agents, should also be considered according to [68]. Halogen-based sanitisers (i.e. sodium hypochloride and iodine-based iodophors) and strong oxidants (i.e. hydrogen peroxide and ozone) can cause severe corrosion damage of stainless steel in contact with process streams. Surfactants (i.e. quaternary ammonium and acid anionic compounds) are expected to be relatively non-corrosive in contact with stainless steel [68].

6 Summary

Degradation of process or storing equipment used in the food industry causes financial inconvenience related to renewing damaged equipment. Stainless steel is found to be the most utilised metal in the food industry, and much literature on corrosion of stainless steel in the food industry has been identified, but also nickel, chromium and titanium alloys have been reviewed. Only a limited number of papers include considerations on health risks from metal release. Allergy to metals is considered to be the main health risk in relation to metal release to food, as more poisonous metals such as lead and cadmium are avoided.

Processes and storing equipment has been reviewed, including metal release from home cookware, cans for food storing, brewing and distilling, crop storage silos as well as cleaning and sanitising procedures. Material degradation in a wide range of food product has been reported, including apples,

pickles, peppers and pepper sauce, butter, asparagus, wine, and glucose.

Papers from a broad variety of types of journals are cited, including papers with a high scientific level as well as papers with focus on industrial aspects. It is the impression of the authors that most often the cited papers are written by authors having expertise in a limited number of areas in the field as for example in either corrosion, wear, food technology or allergy, indicating the need of interdisciplinary work in the field. For instance, guidelines concerning metals and alloys used as food contact materials only take migration into account and do not consider the synergy effect of mechanical action in combination with chemical degradation.

Information describing material degradation in various food products under different process and operating variables can give valuable insight of the parameters involved. An improved understanding of these parameters enhances the opportunities for choosing long-lasting materials. Improved material selection or technological solutions can in the long term reduce expenses because of better products and increased service life of equipment. Furthermore improved material selection will increase food quality and reduce possible metal release.

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Appendix II:

A block-on-ring tribocorrosion setup
for combined electrochemical and
friction testing

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tribo **Test** *A block-on-ring tribocorrosion setup for combined electrochemical and friction testing*

M.S. Jellesen^{*†}, M.Ø. Hansen, L.R. Hilbert and P. Møller

Technical University of Denmark, Department of Manufacturing Engineering and Management, Kemitorvet b.204, DK-2800 Kgs. Lyngby, Denmark

The combined action of corrosion and wear can cause degradation of equipment, and thereby financial losses related to the renewal or repair of damaged equipment. In the food industry, metal degradation is a major concern since metal release eventually can cause health risks for consumers. This study describes a block-on-ring testing facility used to determine sliding wear, and additionally allowing for electrochemical measurements, such as potentiodynamic polarization curves and potentiostatic monitoring of current and potential. To verify the reliability and reproducibility of this block-on-ring tribocorrosion setup, the tribological and electrochemical behaviour of stainless steel sliding against a ceramic ring in sulphuric acid has been determined. Furthermore, a case taken from the food industry has been examined. The study shows that results made on the described block-on-ring testing facility are reliable and can provide improved information about material properties when the material is exposed to combined chemical and mechanical degradation. Copyright © 2007 John Wiley & Sons, Ltd.

KEY WORDS: tribocorrosion; sliding wear; block-on-ring; metal release; food industry

INTRODUCTION

Material failure caused by tribocorrosion can be seen in a number of industries such as mining, mineral processing, chemical processing, pulp and paper production, and energy production. The combination of corrosion and wear can cause continuously metal release from

^{*}Correspondence to: M.S. Jellesen, Technical University of Denmark, Department of Manufacturing Engineering and Management, Kemitorvet, Building 204, Kgs Lyngby, Denmark, 2800.

[†]E-mail: mje@ipl.dtu.dk

equipment. This is a major concern in the food industry since metal release potentially can cause health risks for consumers.¹ Food products can be corrosive due to low pH, high chloride concentrations or high processing temperatures as well as sanitising agents are potentially corrosive.

Premature material failure can occur if materials are chosen from separate determination of wear and corrosion properties. Therefore, it is an advantage to quantify material degradation in parts of corrosion, wear and synergism when performing failure analysis and designing equipment for corrosive tribosystems. This paper shortly introduces tribocorrosion as a degradation mechanism, and describes a block-on-ring tribometer allowing for electrochemical monitoring and control. The test setup has been used for a model system as well as a case taken from the food industry has been examined.

TRIBOCORROSION

Tribocorrosion can be defined as an irreversible transformation of a material caused by simultaneous physicochemical and mechanical surface interactions taking place in a tribological contact.² As indicated in American Society for Testing and Materials (ASTM) Standard G119-93,³ several synergy effects are involved when combining mechanical and electrochemical phenomena.

The total material loss, T , can be considered as in the following equation, where W_0 is the material loss due to wear without corrosion, C_0 is the material loss due to corrosion without wear and S is the material loss due to the total synergism interacting between corrosion and wear.

$$T = W_0 + C_0 + S \quad (1)$$

The total synergism (S) is the sum of the increase of mechanical wear due to corrosion, S' , and the increase of corrosion due to mechanical wear, S'' .

$$S = S' + S'' \quad (2)$$

Electrochemical measurements at constant potential allow mass loss caused by corrosion to be determined from Faradays law.

$$m = n \cdot M = \frac{Q}{z \cdot F} \cdot M \quad (3)$$

The mass loss, m , is found at determination of charge, Q , the number of electrons, z , the molar mass, M and Faradays constant, F .

Figure 1 illustrates how a wear situation removes a passive layer on a surface, and thereby accelerates corrosion.

The increase of corrosion due to mechanical wear, S'' , is most likely seen for passivating metals as indicated in Figure 1. The synergy effect describing increased mechanical wear due to corrosion, S' , can occur if corrosion products are released and then act as third-body wear particles. More obvious is the case where a wear resistant coating is corroding and thereby exposes the bulk metal for wear.

TRIBOCORROSION SETUP

The main function of the described tribometer is to perform tribocorrosion tests of solid parts in sliding motion under the influence of a variety of factors. Laboratory procedures for block-on-ring



Figure 1. Illustration of tribocorrosion occurring on a passivating material, e.g. stainless steel. A passive layer is formed, and then an abrasive particle (or any wear situation) removes the passive layer exposing the bulk material for accelerated corrosion. As the wear situation stops, the surface is allowed to repassivate

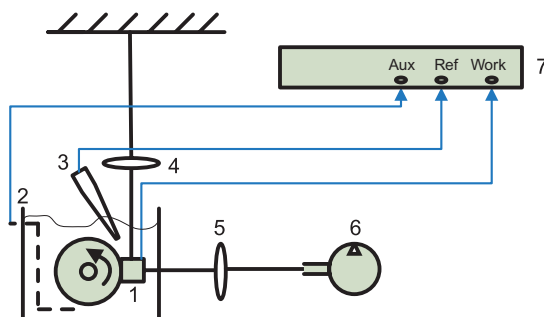


Figure 2. Schematic view of the tribocorrosion setup. 1. Working electrode, 2. Auxiliary electrode, 3. Reference electrode, 4. Strain gauge (F_t), 5. Strain gauge (F_n), 6. Air supply, 7. Potentiostat

wear testing are given in ASTM Standard G77-98.⁴ Friction force, load, electrochemical potential and current measurements are registered during the test. The following factors can be varied and controlled to simulate the actual wear situation being studied.

- Geometry of the block and ring;
- material composition and surface topography;
- chemical environment and potentiostatic monitoring and control of the block;
- load (15–175 N);
- speed (30–3000 rpm);
- temperature.

The rotation of the ring is operated by an electric motor controlled by a sinus-wave frequency control unit in order to avoid vibration. Strain-gauge transducers of oval/hoop shape measures the tangential force (F_t) and the normal force (F_n) used for applying load (Figure 2). The measuring range of the strain-gauge transducers is 2–2500 N. A pneumatic load system is supplied by a standard piston cylinder operating from 15 to 175 N. Other sizes of cylinders can be chosen to provide a broader load range from 100 to 4200 N.⁵

The block-on-ring sliding contact takes place in a box made of polypropylene. When using a ceramic ring, the only metallic parts present in the box are the working and auxiliary electrode. Any risk of interference with the electrochemical measurements is thereby minimised. The reference electrode is fitted to a capillary tube placed approximately 1 cm from the working electrode. Specimens with complicated geometries or with difficulties in thread making can be mounted in epoxy after establishing electrical connection by soldering, and then used as blocks. Such a mounting is shown in Figure 3 to the left. These specimens must be ground thoroughly if several measurements are needed, and the operator must be aware of the risk of crevice corrosion in this case. The simplest

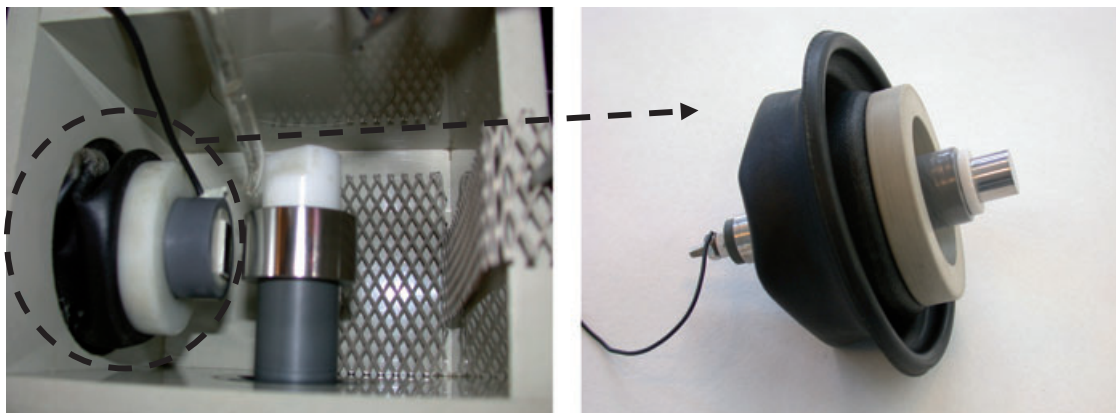


Figure 3. Electrochemical measurements using a standard three-electrode setup in a box, seen from above (to the left). A standard calomel electrode serves as a reference electrode and a net of titanium as counter electrode. The ring shown in this picture is a metallic ring. The working electrode holder used for cylindrical blocks is shown to the right

geometry of the working electrode is cylindrical blocks with a diameter of approximately 12 mm. Such blocks can be attached directly to a holder made of epoxy-coated stainless steel as shown in Figure 3 to the right. A Teflon gasket is placed between the sample and the holder to minimise the risk of crevice corrosion. This holder design gives the possibility of investigating a wide range of materials with ease. The block geometry is the same as indicated in ASTM Standard G5-94.⁶ Once the working electrode holder has been applied to the tribometer setup, it is easy to replace and fasten the blocks without any moulding or soldering required.

MODEL SYSTEM – CERAMIC-RING SLIDING AGAINST STAINLESS STEEL BLOCK

To evaluate reproducibility and compare results of this tribometer with similar experiments made on well documented tribometers,⁷ the following experiments have been performed with replicates of three samples made of certified stainless steel-type American Iron and Steel Institute (AISI) 316L, with a diameter of 12 mm and an exposed area of 5.65 cm².

The materials used were stainless steel-type AISI 316L and alumina (99.9% Al₂O₃) immersed in 0.5 M sulphuric acid at room temperature. This material combination is not likely used in industry, but useful as a model system. The ceramic ring is non-conducting and has a high hardness, and the electrochemical behaviour of stainless steel-type 316L is well characterised. The environment chosen was suitable, since it allowed the stainless steel to passivate, but as a consequence of low pH, a corrosion occurred when the passive layer was removed.

This block-on-ring tribometer simulates sliding wear contact, instead of causing high-local pressure wear situations as in the case of ball on a plate or pin on disc tribometers. Sliding wear is expected to be a more common wear situation than high-local pressure wear situations, since these are deliberately avoided by design. Characteristic factors for the wear situation used in the model system are summarised in Table 1.

Table 1. Test conditions

Ring	Alumina (99.9% Al_2O_3)
Block	AISI 316L
Working electrode area	5.65 cm^2
Motion	Rotating
Wear track length	12 mm
Wear track width	Ranging from 1.51 to 2.28 mm
Exposure	Immersion in 0.5 M H_2SO_4
Load	Air piston, $F_n = 15\text{--}20 \text{ N}$
Ring diameter	22 mm
Rotation frequency	100 rpm
Sliding speed	3.0 m/minute

Table 2. Experiments overview

Experiment 1	Experiment 2	Experiment 3
(a) Polarization curve without wear	(b) Polarization curve with wear	Wear test at OCP
Cathodic polarization	Cathodic polarization	Cathodic polarization
1 mA, 5 minutes	1 mA, 5 minutes	1 mA, 5 minutes
Stabilisation at corrosion potential OCP, 5 minutes	Stabilisation at corrosion potential OCP, 5 minutes	Stabilisation at corrosion potential OCP, 5 minutes
Potential scan from -244 to 1044 mV SHE at a scan rate of 0.5 mV/s	Applied contact and started wear situation for a total of 43 minutes	Applied contact and started wear situation for a total of 48 minutes
	OCP 5 minutes	
	Potential scan from -244 to 1044 mV SHE at a scan rate of 0.5 mV/s	Applied passive potential 744 mV SHE , 15 minutes
		Applied contact and started wear situation, 46 minutes

Polarization curves were performed to determine the kinetics of ongoing reactions, thus the corrosion rate. As a cleaning procedure, the block was cathodically polarised at 1 mA for 5 minutes, and then the open circuit potential (OCP) was monitored. An increased cathodic polarisation current before polarization could have been chosen for a more thorough cleaning of the block surface, but this would increase the risk of hydrogen embrittlement of the block due to excessive hydrogen development. After the cleaning procedure, the polarizations were performed according to the conditions given in Table 2.

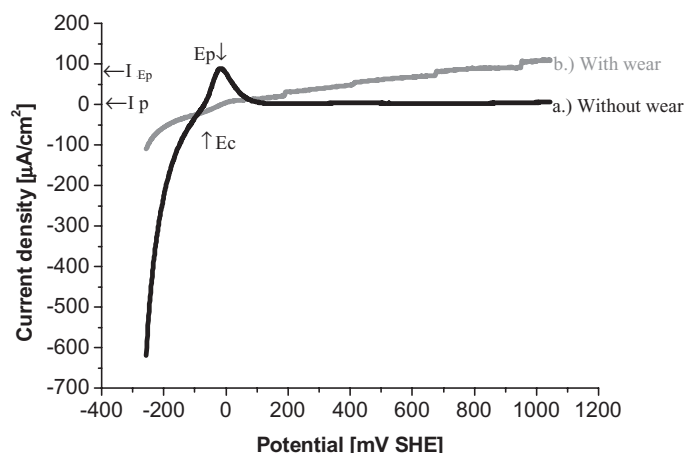


Figure 4. Results from experiment 1a and 1b showing polarization curves of stainless steel 3161 in 0.5 M sulphuric acid with and without wear. The potential scan is ranging from -244 to 1044 mV SHE at a scan rate of 0.5 mV/s

Figure 4 clearly shows the synergy effect of wear on corrosion. As the potential was increased above the corrosion potential (E_c), the stainless steel was in an active region where the dissolution rate of the metal increased until the passivation potential (E_p) was reached. Above the passivation potential, the dissolution rate decreased, and further increase in potential did not affect the dissolution rate. The passive current ($I_p = 3.0 \mu\text{A}/\text{cm}^2$) had a considerably lower value than the critical current density ($I_{Ep} = 90.9 \mu\text{A}/\text{cm}^2$). The passivating range was large, ranging from -16 mV standard hydrogen electrode (SHE) to at least 1044 mV SHE, after which oxygen development was expected.

The polarisation curve registered during the wear situation showed that the electrochemical behaviour of stainless steel was affected by wear in the sense that no passivation potential was reached and no passive region was shown. The current density steady increased as the potential was raised, and the wear track area increased.

A typical wear track is shown in Figure 5.

The polarisation curve shows no evidence of local corrosion. Pitting and crevice corrosion are local corrosion phenomena that may occur on passivated materials. These phenomena are often caused by halogenides present in the surrounding environment, which are not present in this model system environment. The block in Figure 5 does not show any indications of local corrosion. At the end of the wear experiment, the wear track had an area of 0.22 cm^2 . This is a small area compared with the total block area of 5.65 cm^2 ; nevertheless, the current density was remarkably increased as a function of the potential.

The result of experiment 2, a wear test performed while monitoring the OCP, can be seen from Figure 6.

From Figure 6, it can be seen that the potential slightly increased during the first 300 s without wear. This was due to the establishment of a free potential after the cathodic polarisation. As wear started, fresh electrolyte became available and the potential increased until 500 s, whereafter the potential stabilised. As wear stopped, the potential seemed to slightly increase as the OCP was being established. This experiment indicates that the block would passivate in this environment if not exposed to wear. The characteristic factors are summarised in Table 3.

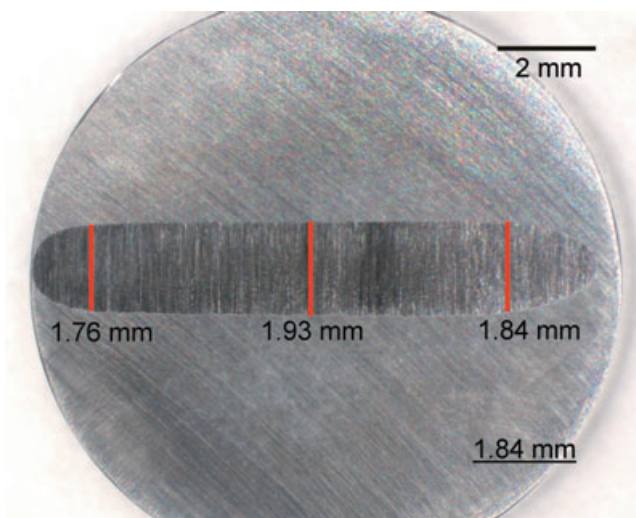


Figure 5. A typical wear track shown for a block used to establish a polarization curve with wear. The average wear track width is given as 1.84 mm (underlined)

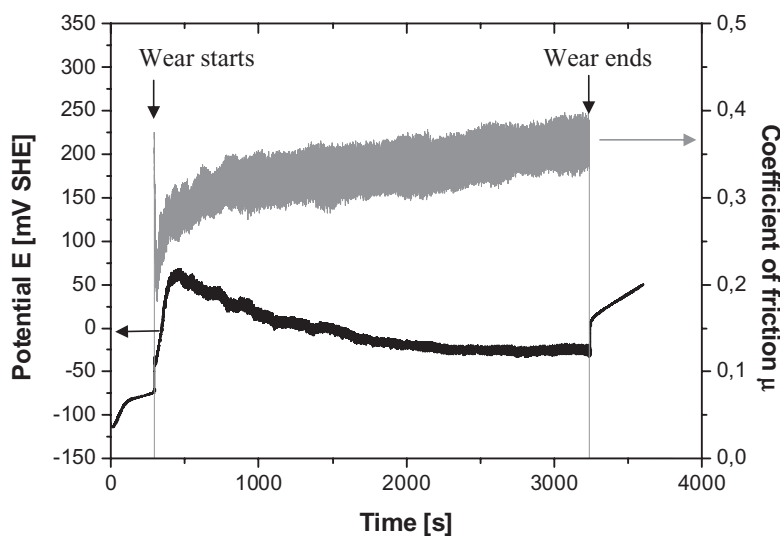


Figure 6. Results from experiment 2 showing how wear influences the OCP. The most representative curve of three repetitions is shown

Table 3. Wear test at OCP

OCP before (mV SHE)	-70
OCP during (mV SHE)	-25
OCP after (mV SHE)	25
Average μ	0.35
Width of track (mm)	1.65
Area track (mm ²)	19.8
Wear volume (mm ³)	0.31

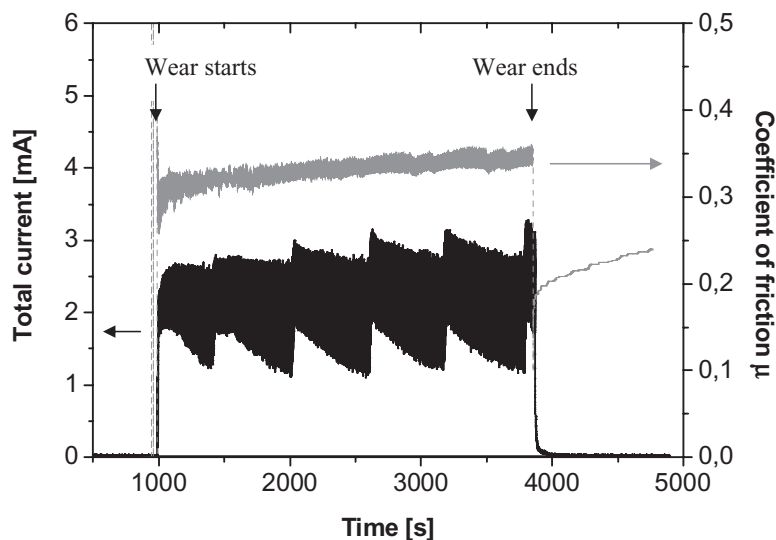


Figure 7. Results from experiment 3 showing the total current and coefficient of friction at an applied potential of 744 mV SHE. The most representative curve out of three repetitions is shown

To study the material loss more quantitatively, a chronoamperometry study at a constant potential of 744 mV SHE has been performed. At this potential, the blocks were held in their passive state. This is illustrated in Figure 7 with a low current registered from 0 to 1000 s.

The effect of wear on corrosion rate is evident, as shown in Figure 7. As wear was applied to the passivated surface, it caused a significant increase in the total current as indicated in the time interval from 1000 to 3800 s. As soon as the ring rotation was stopped, the surface was allowed to repassivate and the current decreased to a negligible level similar to before the ring rotation was started. The high frequency scattering for the experiment shown in Figure 7 was mainly caused by the eccentricity of the ring and, to a lesser extent, caused by vibrations from the motor. The use of air supply at such small loads is also thought to cause mechanical instability causing fluctuations every 600 s. A pilot valve for the air supply was adjusted and it improved the constancy, but still, fluctuations were present. The tribometer has therefore been modified with a weight system to apply load. It has been indicated for a pin on disc apparatus that fluctuations in load will decrease for a dead weight loading instead of pneumatic loading.⁸ Such a modification has recently been made for this block-on-ring setup and results (not shown here) have clearly shown improved stability. Table 4 summarises the characteristic factors for experiment 3, clearly showing the increase in corrosion current from 0.02 mA without wear to 2.5 mA during wear.

Material loss on the block has been determined from its volume loss. This has been done simply by measuring the scar width. With D as the diameter of the ring, b as the average wear track width, θ as the sector angle in radians, it is possible to determine the volume loss from the width of the wear track from the following equation:⁵

$$\text{Volume} = \frac{D^2 \cdot t}{8} (\theta - \sin \theta) \quad (4)$$

where $\theta = 2 \cdot \sin^{-1} \frac{b}{D}$.

Table 4. Chronoamperometry study at applied potential of 744 mV SHE

Current before rubbing (mA)	0.02
Current during rubbing (mA)	2.5
Current after rubbing (mA)	0.02
Average μ	0.35
Width wear track (mm)	2.20
Area wear track (mm ²)	26.4
Wear volume (mm ³)	0.71

Table 5. Mass losses found as an average of three blocks

Experiment	Volume loss (mm ³)	Average volume loss (mm ³)	Time (minutes)	Average mass loss/time (mg/hour)
(1b) Polarization curve with wear	0.42	0.46	43	5.2
	0.46		43	
	0.50		43	
(2) Wear test at OCP	0.24	0.31	48	3.1
	0.27		48	
	(0.23)		(48)	
(3) Wear test and chronoamperometry study at passive potential	0.41	0.71	48	7.4
	0.64		46	
	0.71		46	
	0.79		46	

The volume loss found as an average of three repetitions is given in Table 5. One block is marked with brackets, since it was omitted due to misalignment. Mass loss is calculated using the volume loss and the density of stainless steel, 8.03 g/cm³.

The values in Table 5 are given without statistical deviations, since more replicates are necessary for adequate statistical description. Still, the mass loss values clearly indicated the effect of corrosion, since the mass loss has increased from the wear test at OCP (experiment 2) to the wear test at applied passive potential (experiment 3). The mass loss in experiment 1b, polarisation during wear, was in between the mass losses from experiments 2 and 3, which was also to be expected, due to its middling level of anodic polarisation.

The most valuable experiment performed was experiment 3, where the total current measured at an applied potential easily allowed mass loss due to corrosion to be compared with the total mass loss. The total charge due to corrosion can be estimated and roughly estimates the total corrosion during the 46 minutes of wear. The charge could be converted to mass by using Equation (3).

$$m = n \cdot M = \frac{Q}{z \cdot F} \cdot M = \frac{7.3801C}{2 \cdot 96500C/mol} \cdot 56.4 \text{ g/mol} = 2.2 \text{ mg}$$

Table 6. Quantification of metal release

T [mg]	$W_0 + S'$ (mg)	C_0 (mg)	S'' (mg)
7.4	5.2	0	2.2

This mass loss is the entire corrosion part C_0 and S'' as indicated in Equations (1) and (2). The corrosion part alone (C_0) is determined from the passive current I_{Ep} , as determined by the polarisation curve without wear. This contribution, S' , is most likely negligible in this case and is thus given together with W_0 in Table 6.

A method for exact determination of the S' contribution is to cathodically protect the block during a wear test and then compare the total mass loss with a block allowed to corrode during the wear test. As expected for this model system, the main degradation occurs as a consequence of wear (W_0), but the increase in corrosion due to wear, S'' , has shown also to represent a significant amount of the total material loss (Table 6).

FAILURE ANALYSIS OF EQUIPMENT USED IN THE FOOD INDUSTRY

The effects of tribocorrosion on materials used in processing equipment with metal–metal sliding contact was evaluated by the block-on-ring tribocorrosion setup while performing open cell potential and chronoamperometry studies. The test was performed in 0.21% chloride adjusted to pH 5.6 using lactic acid. This electrolyte simulates the food product being processed. Heat-treated and hardened Sverker 21 is a typically used material for the part here simulated by a ring. Sverker 21 is a high-carbon, high-chromium tool steel alloyed with molybdenum and vanadium, provided by vadeholm and harden to a value of 62 ± 1 Hardness Rockwell Scale (HRC). Examined block materials are low alloy martensitic steel, 80CrV2, with a hardness of 41 ± 1 HRC and high-speed steel, HSS, just hardened to 49 ± 1 HRC.

In order to establish realistic potentials for the chronoamperometry study, the corrosion properties of Sverker 21, HSS and 80CrV2 was studied using electrochemical polarisation as well as potential measurements of the material combinations Sverker21–80CrV2 and Sverker 21–HSS during wear. In the wear situation, the materials became galvanically coupled, and the measured potential was thus a mixed potential originating from both materials. After 2 hours of sliding wear, the potentials of Sverker 21 galvanically coupled to HSS, and 80CrV2 were determined to be -236 mV SHE and -306 mV SHE respectively.

Chronoamperometric studies, similar to those performed in experiment 3 for the model system, were carried out at a potential 20 mV above the measured OCPs during wear. Figure 8 shows the results of Sverker 21 sliding against a block of 80CrV2 and Sverker 21 sliding against a HSS block at 55–65 N loading.

At the starting point of wear, the block is brought into contact with the ring, hereby establishing electrical contact and thus increasing the apparent electrode area. This results in a current increase, being most clear for HSS. During wear, the ring and the block were electrically connected, thus the measured current was the combined corrosion current of the two parts. The exact distribution of these two current contributions was not determined. The abrupt decrease in current occurred as the wear situation was stopped (at 135 minutes), and the physical and electrical contact between the block and ring stopped.

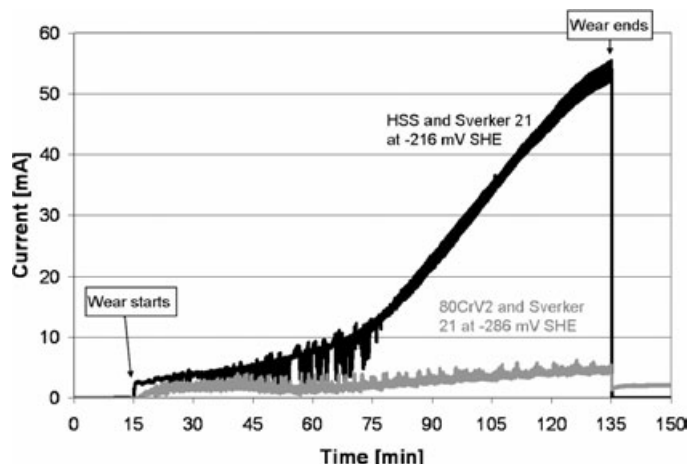


Figure 8. Chronoamperometry of 80CrV2 and HSS against Sverker 21 at 55–65 N load in an electrolyte containing 0.21% chloride adjusted to pH 5.6 with lactic acid. Wear duration is 120 minutes

Table 7. Metal degradation from food processing equipment materials after sliding against Sverker 21 at 55–65 N

Material	Block Average volume loss (mm ³)	Block Average mass loss/time (mg/hour)	Block + ring Total charge, Q (°C)	Block + ring Total corrosion loss, C_0 (mg)
OCP HSS OCP	0.03	0.11		
80CrV2 Chronoamperometry at -216 mV SHE.	0.45 0.03	1.79 0.11	142.8	41.7
HSS Chronoamperometry at -286 mV SHE. 80CrV2	0.82	3.28	20.0	5.8

From Figure 8, the total corrosion charge can be calculated and the total amount of dissolved metal due to corrosion is found by Faradays law Equation (3). The total volume loss due to wear was calculated using Equation (4), by measuring the width of the wear scars on the blocks. These results of 2 hours sliding wear are listed in Table 7.

The mass loss is estimated from the wear track on the block. The mass loss of the ring has not been determined. The total charge and total corrosion loss are given as the sum of distributions from the ring and the block.

Visual inspection of the rings after test has shown that severe local corrosion has taken place for the Sverker 21 ring when sliding against a HSS block (Figure 9). Corrosion products and pitting can be seen in a whirled pattern on the side of the ring. Also, local corrosion in the form of crevice

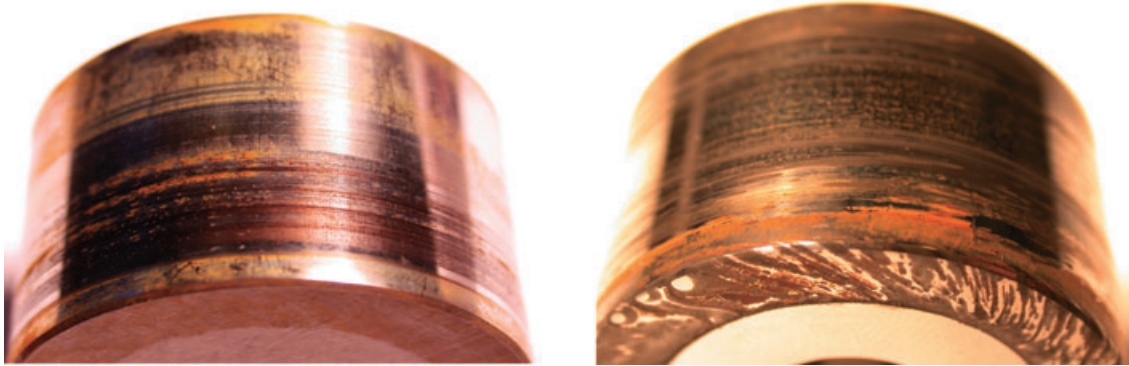


Figure 9. Sverker 21 (ø35 mm) rings after a chronoamperometry study. To the left, a ring after wear against 80CrV2, and to the right, after wear against HSS

corrosion is more severe for the Sverker 21 ring when sliding against HSS rather than 80CrV2. These local corrosion phenomena are probably due to the higher galvanically coupled potential of the HSS and Sverker 21 combination than for the 80CrV2 and Sverker 21 combination. Additionally, the higher hardness of HSS as opposed to 80CrV2 is likely to affect the corrosion properties of Sverker 21, as the HSS block during continuous wear against Sverker 21 more effectively removes passivating oxide layers and other corrosion products (Figure 9).

These experiments show that HSS is a more wear-resistant material than 80CrV2, but when sliding against Sverker 21 in a corrosive environment, the galvanic coupling might accelerate corrosion severely. This increased corrosion is especially occurring for the HSS–Sverker 21 coupling.

CONCLUSION

Experiments with a model system consisting of alumina sliding against stainless steel-type AISI 316L have been performed on a block-on-ring tribocorrosion setup. Experiment 1 clearly showed the effect of wear on the corrosion rate. In experiment 2, the potential was monitored during wear, but this did not provide any information of greater value. Experiment 3, a chronoamperometry study at passive potential, has shown to be the most valuable experiment due to easy quantification of electrochemical material loss.

The results obtained on a block-on-ring tribocorrosion setup have shown to be adequately reproducible and similar to those found for other well-documented tribometer setups. Only one block out of 10 had to be omitted because of misalignment. The coefficient of friction has been determined to be 0.35 for stainless steel against alumina in sulphuric acid independent of the electrochemical conditions. The system needs to be perfectly aligned to avoid asymmetric wear tracks. Symmetric wear tracks are necessary to ensure reliable force measurements and to obtain comparable wear tracks. Ring eccentricity has been measured and is ranging from 7 to 17 μm , which is enough to cause some vibration in the tribosystem. This vibration can be seen in the force measurements. The pneumatic system used for applying load is responsible for most of the fluctuations seen and has since been replaced with a dead weight load system. By the use of grounding and a Faradays cage, electrochemical measurements are possible without interference or electrochemical noise from the surroundings. The electrochemical measurements were performed satisfactorily for both ceramic and

metallic rings. Blocks can be made of cylindrical specimens with thread and more complicated geometries can be wire connected and moulded.

The block-on-ring tribocorrosion setup has been used to evaluate the effects of tribocorrosion on materials used in processing equipment with metal–metal sliding contact. Materials used for equipment in the food industry have been examined. This examination indicates that local corrosion can occur as the block and ring are coupled mechanically and electrically. The wear properties of HSS are expected to be superior to 80CrV2, but when sliding against Sverker 21 in a chloride-containing environment at a slightly raised potential, an unexpected phenomenon occurs. HSS is accelerating local corrosion significantly on Sverker 21, which is causing a considerable metal release.

The use of a block-on-ring tribocorrosion setup has shown to provide valuable information, even though it was not possible to either simulate continuous flow of food product or use exact values of load and electrochemical potential, since these were unknown. A significant increase of corrosion, arising from synergism caused by wear, is clearly indicated and as such, the study shows the importance of determining combined corrosion and wear behaviour of materials used in corrosive tribosystems.

Acknowledgement

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Appendix III:

Corrosion and wear properties of materials used for minced meat production

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CORROSION AND WEAR PROPERTIES OF MATERIALS USED FOR MINCED MEAT PRODUCTION

MORTEN S. JELLESEN, MIKKEL ØSTERGAARD HANSEN,
LISBETH RISCHER HILBERT and PER MØLLER

*Technical University of Denmark
Department of Manufacturing Engineering and Management
Kemitorvet b.204, DK-2800 Kgs. Lyngby, Denmark*

Corresponding author:

*Morten S. Jellesen
mje@ipl.dtu.dk*

ABSTRACT

The risk of material degradation is present in minced meat processing equipment. Corrosion, wear and tribocorrosion properties of commonly used steel materials for such processing equipment are therefore studied. Corrosiveness of minced meat has been evaluated by potentiodynamic measurements. Combined sliding wear and corrosion conditions have been simulated in laboratory using a block-on-ring setup allowing for electrochemical measurements. Detailed information concerning the mechanism of possible material degradation is provided by these results together with microstructural analysis and thermodynamic considerations. Areas of precaution are stated and new material solutions are suggested.

Keywords: Corrosion, Wear, Food industry, Minced meat production, Block-on-ring, Tribocorrosion.

INTRODUCTION

A combination of corrosion and wear can cause continuously metal release from equipment. This is a major concern in the food industry since metal release potentially causes health risks for consumers. (JELLESEN *et al.* 2006). Many food products are known to be corrosive due to low pH and high chloride concentrations (a few of them are shown in Table 1). Also high processing temperatures as well as the use of aggressive sanitising agents are parameters that can accelerate corrosion. Materials used for processing equipment in the food industry can be especially susceptible to combined corrosion and wear, given the lubricant limitations in processing food products. Combined corrosion and wear is termed tribocorrosion and several synergy effects can be involved when combining mechanical and electrochemical phenomena (ASTM STANDARD G119-93, 1998). Thus premature material failure caused by tribocorrosion may occur if materials are chosen from separate determinations of wear and corrosion properties. To optimize material selections and failure analysis of corrosive tribosystems a graduation of total material degradation into parts of corrosion, wear and possible synergism is beneficial.

TABLE 1
SALT CONTENT AND pH VALUES OF VARIOUS FOOD PRODUCTS

Food product	pH	Salt content [mg/100 g]
Milk (cow)	6.40 - 6.80	50
Ketchup	3.89 - 3.92	1042
Mustard	3.55 - 6.00	1252
Lime juice	2.00 - 2.35	1
Vinegar	2.40 - 3.40	1
Minced meat (pork)	5.60 - 6.00	210

(ANON 1962, BRIDGES and MATTICE 1939, SALT 2007).

This work describes corrosion and wear properties of typically used materials for processing equipment when manufacturing minced pork meat added salt and sold in cans. In this process the meat enters a conveyor screw and is processed through a perforated disc by rotation of knives (inserts) in sliding contact with the disc as shown in Fig.1.

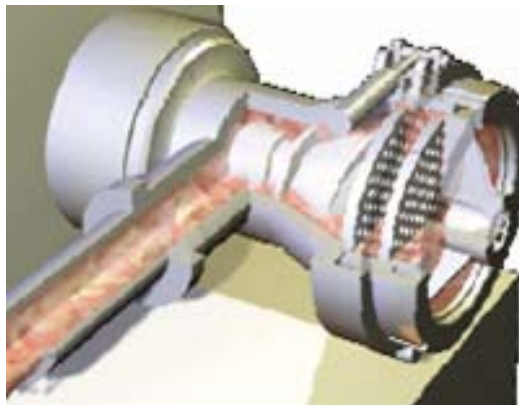


FIG. 1. A TYPICAL SETUP USED FOR MEAT MINCING
IN A CABINET WITH A CONVEYOR SCREW AND
PERFORATED DISCS WITH KNIVES

The knives are rotated in a sliding line contact with the perforated disc, possibly with a thin film of fat, proteins or other constituents from the meat in between. A typical composition of the minced meat mixture investigated for canned meat production is 10-20 wt.% fat added 0.21 wt.% chloride, sodium nitrite, caseinat and various spices. These ingredients are added in the cabinet before mincing. The pH is approximately 6.0 ± 0.2 and the processing temperature below 5 °C.

A typical used material for the perforated disc is Sverker 21 (standard EN 1.2379). Sverker 21 is a high-carbon, high-chromium tool steel alloyed with molybdenum and vanadium (UDDEHOLM 2003). Heat treated and hardened Sverker 21 is the material chosen for many wear applications. An alternative option to Sverker 21 is Vancron 40 which is a nitrided powder metallurgical tool steel (HEIKKILÄ 2002). The rotating knives are commonly made of low alloyed martensitic steel e.g. 80CrV2 (standard EN 1.2235), alternatively high speed steel types alloyed with WC. The cabinet is typically made of stainless steel type AISI 316 L or similar.

MATERIALS AND METHODS

The composition of Sverker 21 and 80CrV2 has been determined by optical emission spectroscopy (OES) and their microstructure examined by light optical microscopy. Hardness measurements have been carried out using the Rockwell hardness test method and conductivity measurements by using a CDM 210 MeterLab[®] conductivity meter from Radiometer analytical. Corrosion properties have been investigated using a Radiometer PGZ301 potentiostat with a Voltalab 4 software. Corrosion experiments were carried out in minced pork meat added 0.21 wt.% chloride as NaCl at a pH of 6.0 ± 0.2 adjusted with lactic acid. Polarization curves are performed according to ASTM Standard G5 (ASTM 1999), all performed at room temperature with a scan rate of 30 mV/min.

Tribocorrosion tests have been performed using a block-on-ring tribometer. The testing of solid parts in sliding motion is in accordance with laboratory procedures for block-on-ring wear testing as given in ASTM Standard G77 (ASTM 1998). Friction force, normal force, electrochemical potential and current are registered during the test. All tribocorrosion tests were performed at a fixed, increased potential since the processing materials are likely to be galvanically coupled to a stainless steel cabinet in the process equipment.

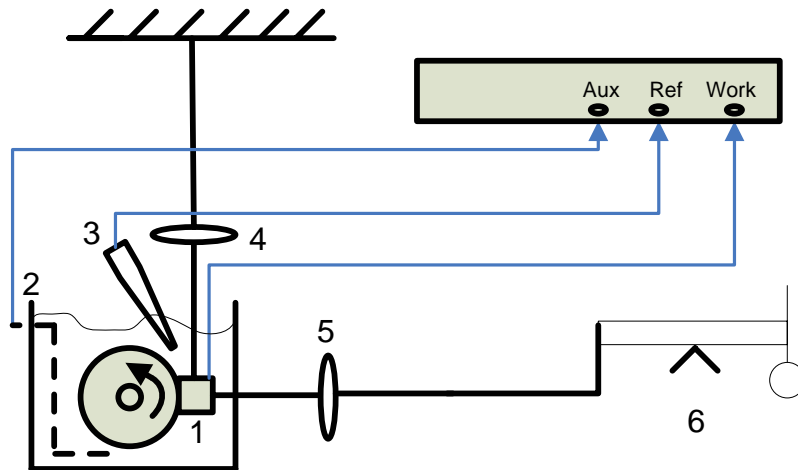


FIG. 2. SCHEMATIC VIEW OF THE TRIBOCORROSION SETUP. 1. Working electrode, 2. Auxiliary electrode, 3. Reference electrode, 4. Strain gauge (F_t), 5. Strain gauge (F_n), 6. Weight load system.

Following factors were kept constant through the tests:

- Normal load is 2 kg.
- All specimen were tested immediately after polishing with SiC grit 500.
- The electrochemical potential is fixed at a value of -156 mV SHE.
- Number of rotations is set to 100 rounds pr. minute.
- Temperature is set at room temperature, 24 °C.

The tribometer setup (Fig. 2) has previously been thoroughly described (JELLESEN 2007) and the reproducibility of the setup has been examined using a model system consisting of an alumina ring in sliding contact with a stainless steel block in dilute sulphuric acid solution. The ring diameter was 35 mm rotating with an eccentricity below 25 μm . The use of a weight load system ensured stabilized conditions for the applied normal force.

A stereomicroscope was used to measure the dimensions of the wear track. After test selected specimens were examined using a scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS).

RESULTS

The wear resistance of tool steels depends on amount, type and size distribution of hard phases as well as the overall hardness. Sverker 21 (from hereof called Sverker), 80CrV2 and Vancron 40 (just termed Vancron) are all martensitic steels, but with a quite different content and distribution of hard phases. The composition of 80CrV2 and Sverker has been determined by optical emission spectroscopy as given in Table 2. The composition of Vancron is given as provided by the material supplier (UDDEHOLM 2007).

TABLE 2
THE COMPOSITION OF TYPICALLY USED MATERIALS FOR MEAT
PROCESSING GIVEN IN wt. %

Material	Fe	Cr	Ni	Mo	Mn	Si	C	W	V	N
80CrV2	Rest (97.7)	0.5	0.1	-	0.4	0.3	0.8	-	0.2	
Sverker 21	Rest(84.4)	11.8	-	0.8	0.4	0.3	1.6	-	0.8	-
Vancron 40	Rest(76.3)	4.5	-	3.2	0.4	0.5	1.1	3.7	8.5	1.8

Sverker and Vancron have been hardened to a value of 62 ± 1 HRC. Vancron is manufactured by hot isostatic compaction of nitrogen atomized, prealloyed high-vanadium powder particles. Knives made of 80CrV2 were delivered from the meat manufacturing industry with a hardness of 41 ± 1 HRC. Measured hardness values are given in Table 3 with an uncertainty of ± 1 , measured with three repetitions.

TABLE 3
HARDNESS OF TYPICALLY USED MATERIALS FOR MEAT PROCESSING

Material	Hardness [HRC]
80CrV2	41 ± 1
Sverker 21	62 ± 1
Vancron	62 ± 1

80CrV2 is typically hardened by oil quenching followed by tempering at relatively high temperature. This results in a martensitic structure, possibly with minor precipitations of chromium carbides. Vancron was hardened by austenitizing at a temperature of 1020°C with 30 minutes holding time followed by quenching and tempering at 560°C (3 x 1 h). This relatively short tempering time is not sufficient to ensure equilibrium and therefore the phase content and composition has been calculated at 1020°C, using Thermo-Calc software (ANDERSSON 2002) with the TCFE3 database. A temperature of 1020°C was also selected when calculating the phases present in Sverker which typically is hardened by austenitizing, quenching and then tempered at 500°C. Data for 80CrV2 is not shown in Table 4, since no distinct precipitation phases are expected.

TABLE 4
COMPOSITION OF PHASES AS CALCULATED BY THERMO-CALC
SOFTWARE

Composition		Elements (wt.%)								
		Fe	W	Cr	Mo	V	C	N	Si	Mn
Vancron	Matrix (78 wt.%)	90,5	1,2	5,0	1,5	-	0,6	-	0,6	0,5
	M(C,N) (17 wt.%)	1,5	0,1	1,4	0,6	76,4	3,8	16,3	-	-
	M ₆ C (5 wt.%)	30,0	36,7	3,9	26,5	0,6	2,2	-	-	-
Sverker	Matrix (85 wt.%)	91,4	-	6,4	0,4	0,2	0,6	-	0,3	0,4
	M ₇ C ₃ (15 wt.%)	32,2	-	51,7	1,8	5,1	8,7	-	-	0,4

Table 4 shows that it is to be expected that Vancron consists of two hard phases; the vanadium-nitride and carbide phases. Vanadium enriched carbides are known to possess

high hardness (KAJINIC 2006). The rest (78 %) is matrix consisting of more than 90 % Fe. It is well known that a corrosion and wear resistant steel must contain excess chromium, since chromium has a high affinity for carbon. The Cr content of the Vancron matrix phase is smaller than for the Sverker matrix and Vancron can therefore be expected to be less corrosion resistant than Sverker in certain environments.

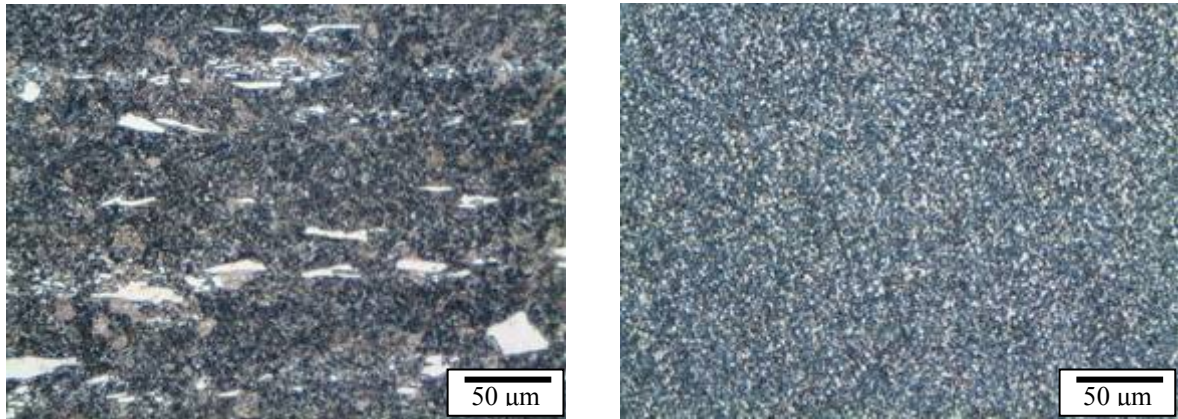


FIG. 3. MICROGRAPHS OF SVERKER (LEFT) AND VANCRON (RIGHT) ETCHED WITH 5 % NITAL SHOWS THE SIZE AND DISTRIBUTION OF HARD PHASES (WHITE)

Besides type and amount of hard phases the wear resistance also depend on the size and distribution of the hard phases (Fig. 3). Sverker contains approximately 15 wt.% of M_7C_3 (M is mainly Cr) as the hard phase, coarsely distributed as long and flat precipitates. This results in a lower volume fraction of hard phases than for Vancron, where the hard phases are finely distributed as small spheres, creating a larger contact area for tribological contact. The microstructure and tribological behaviour of Vancron has previously been studied, showing that it has a high volume fraction of evenly distributed carbonitrides thus supplying a large area for the tribological contact (HEIKILLÄ 2004). Therefore it is expected that Vancron is a more wear resistant material than Sverker, but in order to show how Vancron will perform under combined corrosion and wear, both corrosion and tribocorrosion investigations have been performed as presented in the following.

Corrosion results

Minced pork meat (10-12 % fat) made for consumers, was blended with a household hand blender and 0.21 wt.% chloride was added. The mixture is still highly viscous after blending and has a conductivity of 8.6 mS/cm^2 at 23°C and a pH value of 6.0 ± 0.2 . Given the relatively high conductivity, ohmic drop compensation in the electrochemical data has not been performed. All specimens were polished with SiC grit 500 before testing.

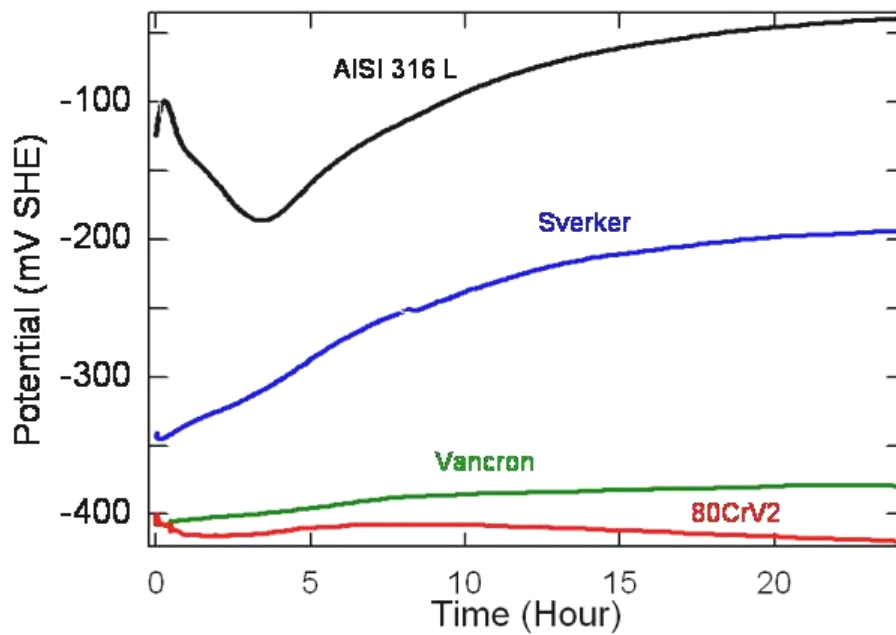


FIG. 4. OPEN CIRCUIT POTENTIAL 24 MONITORING IN MINCED MEAT ADDED 0.21 WT.% CHLORIDE

After 24 hours of open circuit potential (OCP) monitoring (Fig. 4) it can be seen that 80CrV2 has the lowest OCP of the three wear resistant materials. The OCP value increases noticeably for Sverker, probably due to passivation, whereas Vancron and 80CrV2 remain at a low value. The OCP value of AISI 316 L decreases the first few hours, but then it increases to a final value of approximately -50 mV SHE.

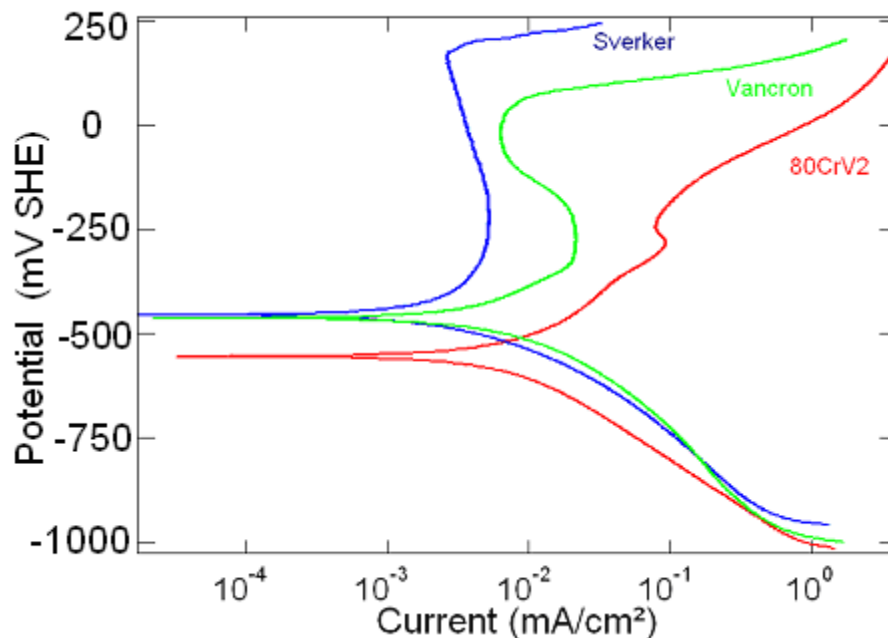


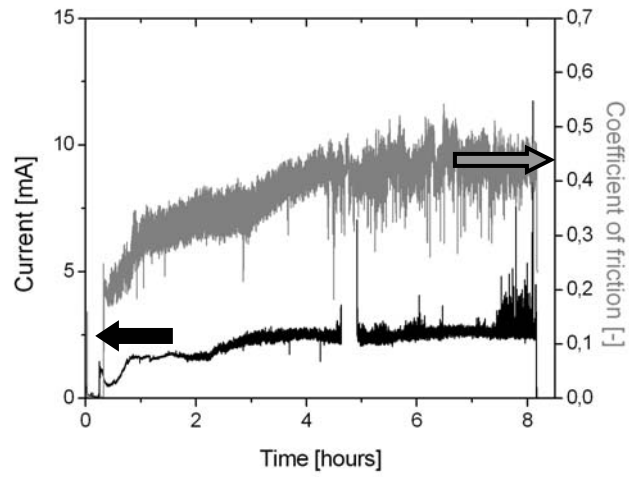
FIG. 5. POLARIZATION CURVES IN MINCED MEAT ADDED 0.21 WT.% CHLORIDE, PERFORMED AT ROOM TEMPERATURE WITH A SCAN RATE OF 30 mV/MIN.

The polarization curves (Fig. 5) show that Sverker has a corrosion potential of approximately -450 mV SHE and maintains a passive area until 200 mV SHE where local corrosion initiates. Vancron shows a smaller passive area and breakdown begins already at 100 mV SHE. 80CrV2 shows no sign of passivation and corrodes uniformly throughout the potential scan with a corrosion potential of -550 mV SHE.

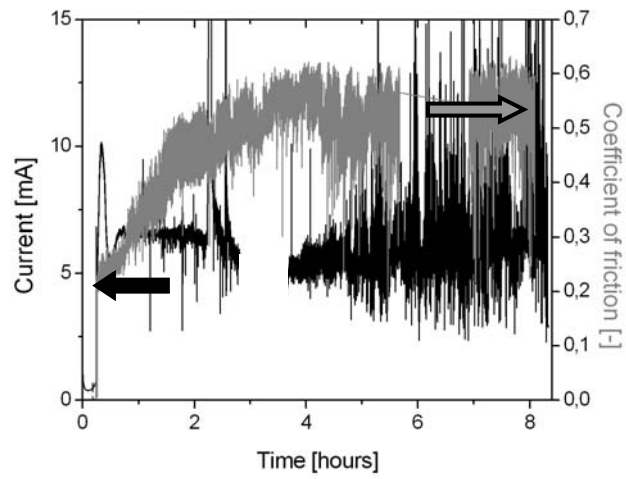
Tribocorrosion results

The fixed potential, used for tribocorrosion testing, is chosen as -156 mV SHE (-400 mV SCE) since stainless steel is expected to raise the potential of the other materials when galvanically coupled (Fig. 4). The validity of the fixed potential value chosen is not certain and investigations are ongoing to evaluate its exact value in process equipment during operation. The potential value is of great significance, since corrosion rates clearly accelerates (Fig. 5) when increasing the potential for these (relatively non corrosion resistant) materials investigated.

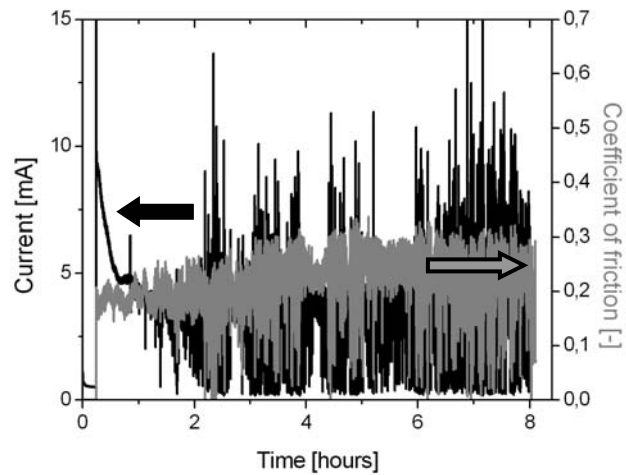
The block and ring was aligned in the tribometer for tribocorrosion testing (Fig. 2) and 1 kg minced meat was added. A lid was placed on top of the meat. It provides pressure to ensure that the wear contact was enclosed by meat. The coefficient of friction (COF) and the resulting corrosion current is shown for 3 different material couplings in Fig. 6. First the typical material coupling (Sverker against 80CrV2) was tested, then one part was replaced by Vancron and finally both parts were replaced by Vancron.



i.) Sverker ring against 80CrV2 block



ii.) Vancron ring against 80CrV2 block



iii.) Vancron ring against Vancron block

FIG. 6. COEFFICIENT OF FRICTION AND ELECTROCHEMICAL CURRENT AT A FIXED POTENTIAL OF -156 mV SHE IN MINCED MEAT ADDED 0.21 WT.% CHLORIDE FOR 3 DIFFERENT MATERIAL COUPLINGS SLIDING WITH A LOAD OF 2 KG

After approximately 2 hours all curves show fluctuations in the resulting corrosion current, especially when Vancron is involved. Probably local corrosion is initiated and propagating at this time. This can affect the wear situation and cause the scattering of COF. The temperature of the meat was monitored. The highest temperature increase registered was for the Vancron ring sliding against a 80CrV2 block with an increase from 18 °C to 30 °C (room temperature was 24 °C). These temperatures are higher than in actual processing. The corrosion rate is thus expected to be lower in actual processing with temperatures below 5 °C.

TABLE 5
TOTAL MATERIAL LOSSES FOR DIFFERENT MATERIAL COMBINATIONS
TESTED IN MINCED MEAT

Material coupling	Block material loss (wear track) [mm ³]	Ring material loss (total) [mg]	Avg. COF [-]	Total current (ring and block) [mA]
<i>Sverker ring against 80CrV2 block</i>	0.51	0.2	0.44	2,5 +/- 1
<i>Vancron ring against 80CrV2 block</i>	2.09	17.1	0.53	5 +/- 5
<i>Vancron ring against Vancron block</i>	0.08	31.2	0.25	5 +/- 5

The material loss of the ring includes loss by both corrosion and wear on the entire ring surface, since it is based on mass determinations before and after the test. It is important to notice that the material loss for the block is determined only by measuring the wear track dimensions as shown in Fig. 7 and then calculating it into volume loss. This means that any material loss, due to corrosion outside the wear track of the block, is not included in Table 5. If material loss due to corrosion is estimated from the curves given in Fig. 6 it will actually exceed the total material losses given in Table 5, since local corrosion can take part on the block outside the wear track. Coating of the block area not exposed to wear could reduce this effect.

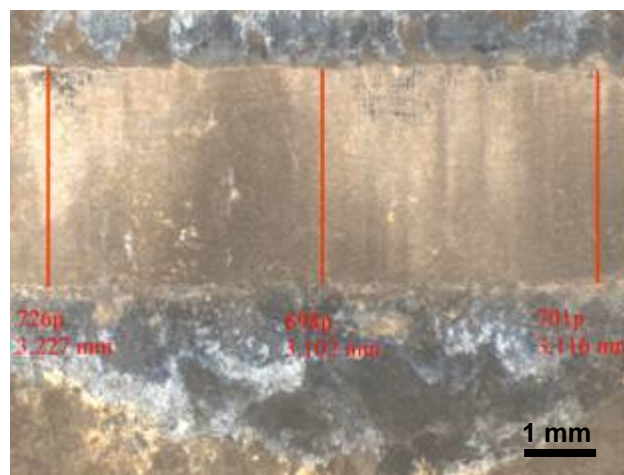


FIG. 7. WEAR TRACK ON 80CrV2 AFTER SLIDING AGAINST VANCRON IN
MINCED MEAT ADDED 0.21 WT.% CHLORIDE WITH A 2 KG LOAD AT - 156 mV
SHE

The characteristics of the different material couplings can be summarised:

○ *Sverker ring against 80CrV2 block:*

The material loss for the ring was significantly small when using this material combination. Visual inspection showed no sign of corrosion on the Sverker ring and only minor signs of wear were visible. This was expected since the ring is harder than the block. Corrosion attacks were visible above and beneath the wear track on the block.

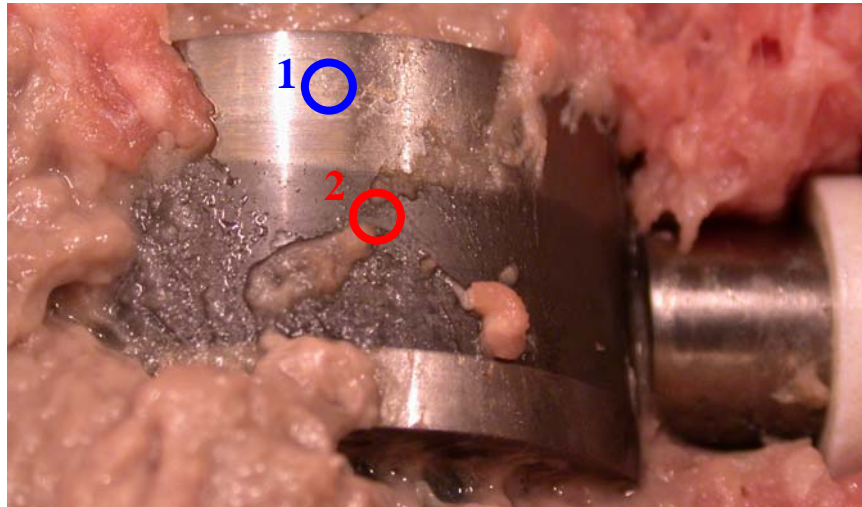
○ *Vancron ring against 80CrV2 block:*

The ring as well as the block showed large material losses. The block shows the largest wear track of the material combinations tested and both block and ring show signs of local corrosion.

○ *Vancron ring against Vancron block:*

Visual inspection showed that the large material loss for the ring is due to corrosion outside the wear contact. The wear track on the block was small, but the block had also suffered from local corrosion outside the wear track. The coefficient of friction was remarkably low throughout the test and a black layer adhering to the surface of the ring had been formed.

The chemical composition of the layer formed on Vancron was analyzed with EDS. The examined areas are shown in Fig.8.



Wt. %	C	N	O	V	Cr	Fe	Mo	W	Mn	Si
1	(4.7)	(2.1)	(5.1)	18.8	8.9	45.3	7.5	7.7	-	-
2	(5.7)	(1.9)	(9.6)	23.5	12.4	31.0	8.4	7.6	-	-
Bulk	1.1	1.8	-	8.5	4.5	76.3	3.2	3.7	0.4	0.5

FIG. 8. AFTER 8 HOURS OF SLIDING WEAR BETWEEN A VANCRON BLOCK AND A VANCRON RING IN MINCED MEAT AFTER REMOVAL OF THE TOP LAYER OF MEAT. VALUES FROM EDS STUDYING ARE GIVEN.

The EDS analysis indicates that Fe is being removed as a result of the sliding wear contact and that the black layer formed is enriched in V, Cr and Mo. Similar black layers were not seen for any of the other material combinations. It should be noted that the EDS analysis is inaccurate in detection of C, N and O and that more accurate quantitative analysis is possible using other techniques. In the SEM investigation of Vancron before wear it was possible to point out the matrix phase as well as a chromium and a vanadium rich phase and they were both evenly distributed as small segments in the matrix phase.

DISCUSSION

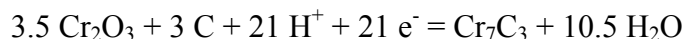
Investigations of the corrosion resistance have shown that 80CrV2 has the lowest OCP of the three materials. The OCP value increases noticeably for Sverker due to its passivation during monitoring. Polarization curves show that Sverker has the largest passive area, but local corrosion will initiate at higher potentials. Vancron shows a small passive area with a breakdown, due to local corrosion, at a lower potential than Sverker. 80CrV2 shows no sign of passivation and corrodes evenly throughout the potential scan.

A block-on-ring tribocorrosion setup was used to evaluate corrosion-, wear- and synergy-parts of metal degradation taking place. Even though a lid ensured that meat will enclose the wear contact at all times, it is not possible to simulate the flow of meat that exists in the actual processing at the meat plant. All tribocorrosion tests were performed at a fixed, increased potential since the materials and meat are in contact with stainless steel in the process equipment. The validity of the potential value chosen is not certain and investigations are ongoing to evaluate its exact value in process equipment. The potential value is of great significance, since corrosion rapidly accelerates when increasing the potential for the materials investigated.

The tribocorrosion testing has shown that corrosion contributes significantly to the total material loss with the elevated potential and limited tonnage given when laboratory testing. Sverker outperforms Vancron in respect of corrosion properties, but Vancron show a remarkably low coefficient of friction when sliding against Vancron itself.

Since 80CrV2 mostly consists of iron there will be a great risk of adhesive wear if the iron containing matrix will be dominant in tribological contact (as the case is for Sverker with a iron containing matrix phase of 85 %) since iron and iron will have a tendency to adhere together. This causes a higher coefficient of friction when Sverker or 80CrV2 are involved and may explain the remarkably low coefficient of friction for Vancron sliding against Vancron with a iron matrix of 78 % and a size and distribution of hard phases minimizing the iron iron contact. Several atomic-level effects have been reported likely to improve antigalling characteristics of such a VN–Fe interface (VITOS 2006).

The corrosion properties of such precipitated hard phases can be described by a Pourbaix diagram. Fig. 9 shows how Cr_7C_3 will transform into Cr_2O_3 at relatively low potentials.



During a wear situation Cr_2O_3 is not expected to form a wear resistant layer and will be mechanically removed. This mechanism can result in less corrosion and wear resistance than expected.

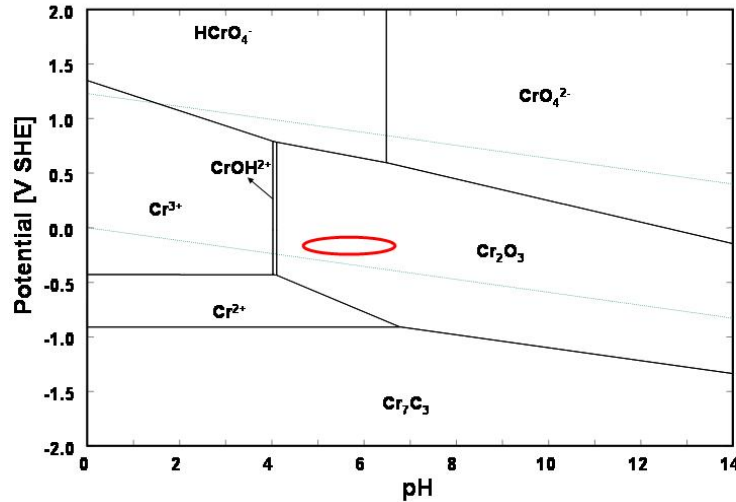


FIG. 9. POURBAIX DIAGRAM FOR Cr_7C_3 AT $1 \cdot 10^{-6} \text{ M Cr}$ AND $1 \cdot 10^{-3} \text{ M C}$ AT 1 BAR AND 25°C

The pH value may vary close to the surface due to local corrosion processes or due to the degradation of meat. The potentiostat is keeping the potential constant at a value of -156 mV SHE , but the exact value of the actual electrochemical potential the materials are exposed to during actual processing and cleaning procedures during use can vary from this value.

CONCLUSION

The processing of food products often requires corrosion resistant processing materials, due to low pH, high salt content and high processing temperatures. Materials used for processing meat into minced meat also need to be wear resistant, since this process involves mechanical interactions like the sliding wear contact between materials or the interaction of abrasive particles like possible bone particles or wear debris.

The presented corrosion results clearly indicate that local corrosion can occur in minced meat added salt and that thoroughly cleaning, rinsing and drying is an area of precaution if corrosion is to be avoided for typically used process equipment materials used in the food industry.

Tribocorrosion results indicate that a perforated disc made of Vancron as an alternative to Sverker is expected to have a remarkably lower coefficient of friction. Whether or not it will corrode depends on the potential of the actual process equipment and the cleaning procedures being used. Vancron is now being tested as a process equipment material for mincing meat and is being surveyed by measuring metal content in minced meat before and after the processing step involving Vancron.

The block on ring tribocorrosion testing facility has its limitations when compared to tonnage and process conditions at full industrial scale, but it gives the possibility for testing and comparing various materials and surface modifications under well controlled conditions. Improvement of materials selection for processing equipment can happen through such better understanding of failure mechanisms and improved testing methods. This will benefit suppliers and users of processing equipment, as well as consumers of food products, since it will contribute to ensure a safe food supply.

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Appendix IV:

Erosion-corrosion behavior of innovative hardening treatments and coatings on stainless steels for food industry applications

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Erosion-Corrosion Behavior of Innovative Hardening Treatments and Coatings on Stainless Steels for Food Industry Applications

Morten S. Jellesen,^{1*} Mads K. Hansen,² Lisbeth R. Hilbert¹ & Per Møller¹

¹Technical University of Denmark, Lyngby, Denmark; ²Danish Technological Institute, Aarhus C, Denmark

A corrosive environment, wear and a combination of the two degradation mechanisms is a possible cause of material degradation of process equipment used in the food industry. Material degradation causes metal release which is a possible health risk for consumers. Many food products are known to be corrosive and therefore stainless steel is the most commonly used material. Stainless steel is known for its corrosion resistance, but due to its poor tribological properties, there is a risk of material degradation when exposed to combined corrosion and wear. The aim of this study was to investigate the role of innovative hardening treatments and coatings on stainless steel. Electrochemical measurements have been performed in a food simulant under impingement conditions with suspended alumina particles.

Keywords: Coatings on stainless steel, surface hardening treatments, corrosion, tribology, thin films

Introduction

Stainless steel is often used in the food industry because of its excellent corrosion resistance. Stainless steel is also known to have poor tribological properties and material degradation is likely to occur when wear and corrosion is combined. Erosion-corrosion is a combined mechanism by which materials suffer damage due to combined erosion and corrosion. Examples of erosion-corrosion failures in the food industry are described elsewhere.¹

Erosion-corrosion is a subgroup of tribocorrosion and is as such dominated by two mechanisms: electrochemical corrosion and mechanical wear. When an interaction between the electrochemical and mechanical processes becomes significant, it will cause material failure earlier than expected. Nitriding of stainless steel is a hardening treatment known to enhance wear resistance, but only a small amount of work has been published concerning the tribocorrosive behavior of nitrided stainless steel.

The present work investigates the erosion-corrosion properties of stainless steel type AISI 316 L. The effect of surface modifications such as low temperature nitriding and coating with diamond-like thin films (DLC) has also been investigated. The erosion-corrosion properties are determined using online electrochemical measurements.

Tribocorrosion

Material failure caused by tribocorrosion can be seen in a number of industries, such as mining, mineral processing, chemical processing, pulp and paper production and energy production. In the food industry, tribocorrosion is also a possible degradation mechanism. Some food products can be corrosive due to their low pH, high chloride concentrations, high processing temperature as well as cleaning and sanitizing agents, which can be corrosive. The combination of corrosion and wear can cause continuous metal release from process equipment, which is a major concern in the food industry since metal release eventually can cause health risks for consumers.¹

Approximate pH values and salt contents of various food products are shown in Table 1.^{2,4} Parameters such as processing temperature and the existence of abrasive particles (pips from the vegetable itself or contaminants, e.g., grits from harvesting) are likely to influence the corrosion and wear properties of materials used for process equipment.

Tribocorrosion can be defined as an irreversible transformation of the material caused by simultaneous physicochemical and mechanical surface interactions taking place in a tribological contact.⁵ As indicated in ASTM Standard G119, several synergistic effects are involved when combining mechanical and electrochemical phenomena.⁶

The total material loss, T , can be considered as in the following equation, where W_0 is the material loss due to wear without corrosion, C_0 is the material loss due to corrosion without wear and S is the material loss due to the total synergy interacting between corrosion and wear.

$$T = W_0 + C_0 + S \quad (1)$$

The total synergy (S) is the sum of the increase of mechanical wear due to corrosion, S' and the increase of corrosion due to mechanical wear, S'' .

* Corresponding author:

Morten S. Jellesen

Department of Manufacturing Engineering and Management

Technical University of Denmark

Kemitorvet b.204

DK-2800 Kgs. Lyngby, Denmark

E-mail: mje@ipl.dtu.dk

Table 1
Approximate pH and salt content of various food types²⁻⁴

Food product	pH	Salt content, mg/100 g
Milk, cow	6.40 - 6.80	50
Ketchup	3.89 - 3.92	1,042
Mustard	3.55 - 6.00	1,252
Lime juice	2.00 - 2.35	1
Vinegar	2.40 - 3.40	1

$$S = S' + S'' \quad (2)$$

Electrochemical measurements at constant potential can roughly quantify mass loss caused by corrosion, since mass loss by approximation is related to charge (and thus the measured current) as described by Faradays law.

$$m = n \cdot M = \frac{Q}{z \cdot F} \cdot M \quad (3)$$

The mass loss, m is found from a determination of charge, Q , and using the number of electrons, z , the molar mass, M and Faraday's constant, F .

The increase in corrosion as a consequence of wear (S'') is illustrated in Fig. 1. The synergy effect describing the increased mechanical wear due to corrosion, S' , can occur if the corrosion products are released and then act as third body wear particles. More obvious is the case where a wear-resistant coating is corroding and thereby exposing the bulk metal to wear.

As a consequence of erosion-corrosion, premature material failure might occur if materials are chosen on the basis of separate determination of wear and corrosion properties. Therefore it is an advantage to quantify the relative contributions to material degradation from corrosion, wear and synergy when performing failure analysis and designing process equipment for corrosive tribosystems.

The electrochemical processes can be monitored by sensitive electrochemical measurements in an erosion-corrosion setup as described in this paper. Such measurements provide further insight into the corrosion related mechanisms in relation to previous examinations based only on weight loss description. Materials applicable for the industry are examined in a flow of fluid and suspended particles and monitored by electrochemical measurements, such as potentiodynamic polarization curves and potentiostatic monitoring of current and potential.

Materials and methods

In this work the corrosion and erosion-corrosion properties of AISI 316 L stainless steel were studied in a food product simulation solution. The effect of low temperature nitriding of AISI 316 L stainless steel was also studied. Furthermore, diamond-like carbon (DLC) coatings were evaluated as stand-alone coatings on stainless steel and as an additional coating on nitrided stainless steel. The reason for studying the last combination was to obtain information concerning the relationship between erosion-corrosion and improved hardness of the base material - in principle studying the corrosion properties as a consequence of improved mechanical resistance to non-elastic deformation.

AISI 316 L stainless steel

Specimens, made from wrought stainless steels, were machined and polished to a final dimension of 15×15 mm with a wall thickness of 2 mm. All AISI 316 L specimens were polished to grit 4000 using SiC paper. Before the specimens were exposed to erosion-corrosion they were passivated in a 25 wt% solution of nitric acid for 30 min at room temperature. The composition of AISI 316 L stainless steel has been determined by OES and is given in Table 2.

Plasma and low temperature nitriding

Conventional plasma nitriding is known to improve the tribological properties of stainless steel, but at the expense of lowering the corrosion properties. This is caused by the high ($>475^\circ\text{C}$) nitriding temperature used in conventional nitriding, causing chromium to precipitate as chromium-carbides/nitrides and thereby decreasing the chromium content locally in the matrix.⁷ A study of a conventional plasma nitriding process taking place at 500°C for 20 hr shows chromium nitride precipitation and thus very poor corrosion resistance.⁸ In the present study we investigated a plasma nitriding process at 485°C for 18 hr. An alternative to conventional nitriding is low-temperature nitriding.⁹ This is a gaseous process for synthesizing a surface layer of expanded austenite with high hardness and apparently without influencing the corrosion properties of stainless steel, since chromium is not depleted from the matrix. A cross section of the surface layer is shown in Fig. 2 indicating a layer depth of approximately 7 to 8 μm .



Figure 1—Illustration of tribocorrosion (erosion-corrosion) occurring on passivating materials, e.g., stainless steel. A passive layer is formed and then an abrasive particle removes the passive layer, exposing the bulk material for accelerated corrosion. The surface might repassivate as the solid particle abrasion stops.

Table 2
Composition of AISI 316 L stainless steel given in wt%

	Fe	Cr	Ni	Mo	Mn	Si	C	P	S	V
316L	68.9	16.7	10.1	1.9	0.9	0.4	0.03	0.08	0.03	0.1

After polishing, the specimens were heat treated at austenitizing temperature (1080°C) performed in a thermo weight as described elsewhere.¹⁰ The nitriding process was done in a gas flow consisting of 30 mL/min NH_3 , 20 mL/min H_2 and 5 mL/min N_2 . The system was heated at 10°C/min up to 445°C and this temperature was held for 20 hr.

The effect of hardening was tested using a Futuretech FM 700 microhardness tester. A Vickers diamond was applied to the cross-section with a load of 5 g. Seven repetitions were made across the cross-section. The results are presented in Table 3.

DLC and DLC-duplex multilayer coating

DLC films show such properties as electrical insulation, low friction in sliding wear situations, high wear resistance, high hardness and electrochemical inertness. The term diamond-like carbon describes a mixed structure of various forms of carbon atoms with different sp^3 and sp^2 bonding proportions depending on deposition technique and parameters. The composition of various C-H alloys can be presented as in Fig. 3.¹¹ The sp^3 bonds form the tetrahedral structure of diamond, whereas graphite consists of sp^2 bonds.

The two coating systems investigated in this work are illustrated in Fig. 4: (1) a DLC thin film on AISI 316 L and (2) a DLC-duplex multilayer coating on AISI 316 L.

The superior mechanical performance and corrosion resistance for DLC films makes it the preferred candidate for protective films in many situations. However it is difficult to obtain good adhesion to steel substrates. In this work both coatings were a:C-H (amor-

phous hydrogenated carbon) layered on an AISI 316 L substrate with an intermediate adhesion layer consisting of a functional gradient coating (FGC) for improved adhesion. The DLC-duplex multilayer coating had a sublayer of conventional plasma nitriding (approximately 40 μm thickness). The plasma nitrided sublayer improves the substrate hardness and supports the top layer when exposed to mechanical impacts. Such a multilayer system has been shown to improve wear resistance in cases when corrosion has not been involved.

The erosion-corrosion testing facility

Our erosion-corrosion test setup made it possible to study and compare the erosion-corrosion properties of different materials under simultaneous corrosion and solid particle erosion in a turbulent flow. The test setup allowed for corrosion control and monitoring and was similar to the impinging jet apparatus described elsewhere.^{12,13} It consisted of a working electrode (the test specimen), an auxiliary electrode (a titanium net) and a standard reference electrode (saturated calomel electrode, SCE) connected to the solution by salt-bridging. The three electrodes were connected to a potentiostat as shown in Fig. 5.

Specimens were machined to a final dimension of 15 × 15 × 2 mm and polished, then appropriately cleaned and dried. The specimen was placed in a holder which exposed an area of 1.64 cm^2 and established contact via a gold plated spring on the backside of the specimen. One kg of 250- μm Al_2O_3 particles was placed in the 60-L tank. An agitator stirred the particles to a certain extent. A hose connected to the suction side of the pump processed particles and

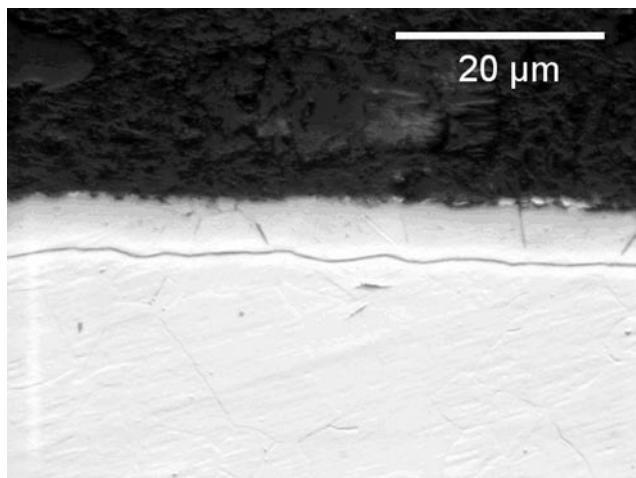


Figure 2—Light optical microscopy picture of the cross section of low temperature nitrided stainless steel. The cracks in the layer can be caused by the preparation, due to the brittleness of the layer. The surface was polished to 1- μm finish and was etched with HCl/HNO_3 solution for 30 sec.

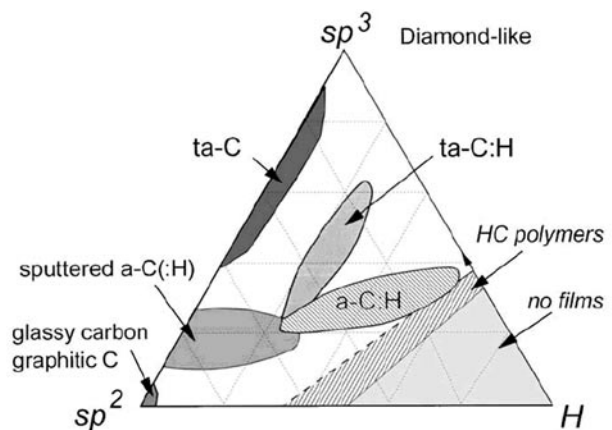


Figure 3—Various forms of bonding in C-H alloys presented in a ternary phase diagram.¹¹

Table 3
Microhardness measurements of the cross section of low temperature nitrided AISI 316 L

Material	Average Hardness, HV _{5g}
Untreated AISI 316 L	275 ± 8
Conventional plasma nitrided AISI 316 L	839 ± 29
Low temperature nitrided AISI 316 L	1160 ± 11

liquid through the pump and the jet impinged on the specimen at an angle of 90°. After impingement, the particles dropped to the bottom of the tank, where they were circulated again. By adjusting the position of the particle connection hose it was possible to vary the quantity of particles in the jet. The highest particle amounts were obtained when the hose was closest to the bottom. It was also possible to adjust the stirring velocity, which had an effect on the particle content. The setup was equipped with an outlet for determining the particle content. One-liter samples were examined by particle filtering and weight determination. The reproducibility was adequate and the equipment was capable of delivering particle loads from 0 to 9 g/L. The pump used was a diaphragm pump driven by air. The pump contained only a few metal parts and the valve balls and seats were inevitably worn after many hours of service, but could be easily replaced.

The solution was kept at room temperature (22 to 23°C) and stirring was performed during all experiments. The pump was set to deliver 6.0 L/min and the nozzle had a diameter of 6 mm, resulting in a liquid velocity of 5.2 m/sec. With the given flow rate and the viscosity, the jet had a turbulent flow according to the Reynolds number. The distance between the specimen and the jet nozzle was fixed at 5 mm. All the parameters can be seen in Table 4.

In this study the solution consisted of 40 L of 0.05M sodium citrate/citric acid buffer at pH 4 with a sodium chloride concentration of 0.5 wt% as a simulant for a food product. Also a solution simulating tap water was used to study the effect of erosion on

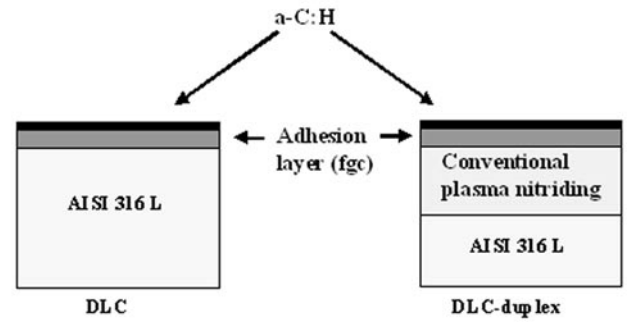


Figure 4—Schematic illustration of DLC and DLC-duplex multilayer coatings.

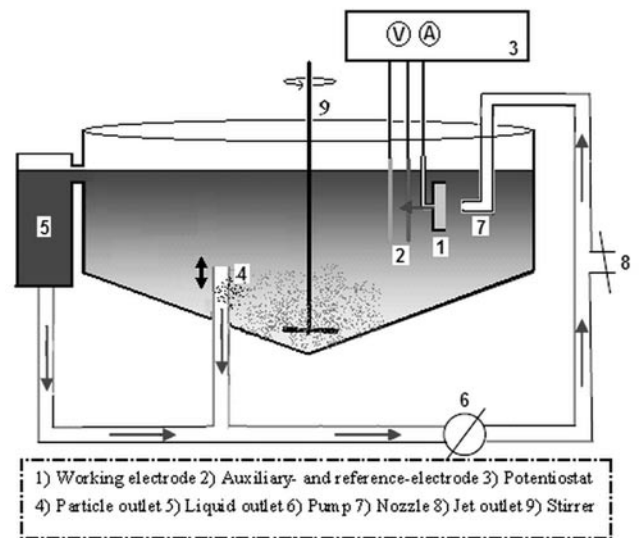


Figure 5—Erosion-corrosion experimental setup.

stainless steel in such a mildly corrosive solution. Dynamic electrochemical measurements such as polarization sweeps and potentiostatic monitoring of current at a fixed potential were performed.

Microscopy of the eroded specimens was performed using light optical microscopy and scanning electron microscopy (SEM). Non-destructive laser measurements were performed to study the topography on some selected eroded specimens.

Table 4
Erosion-corrosion parameters

Specimen	Particles	Solution	Process parameters
AISI 316 L	Al ₂ O ₃ size, 250 μm	0.5% NaCl - NaAc / citrate buffer	6 L/min = 5.2 m/sec
Low temp. nitrided AISI 316			90°
DLC		pH 4.0	0.6 g/L
DLC-duplex			5 mm distance

Results

The effect of erosion on AISI 316 L stainless steel was investigated using dynamic electrochemical measurements. The effect of low temperature nitriding was determined by monitoring the open circuit potential during erosion-corrosion. For untreated, DLC and DLC-duplex coated AISI 316 L, potentiostatic monitoring of the current at a fixed potential was done.

The effect of erosion on the corrosion resistance of stainless steel

To investigate the influence of erosion in a low chloride-containing solution, polarization curves were performed in tap water simulating solution with and without 0.35 g/L particles as shown in Fig. 6.

Figure 6 shows that the corrosion potential decreased by about 100 mV under erosive conditions. The corrosion current density could be estimated by the use of Tafel slopes at a value of $0.01 \mu\text{A}/\text{cm}^2$ under pure corrosion and $0.1 \mu\text{A}/\text{cm}^2$ during erosion-corrosion. As a consequence of the erosive wear, the corrosion rate increased by a factor of ten. The solution used in this experiment was 0.03 wt% chloride, which corresponded to the limit value of chloride in Danish drinking water. This solution simulated a mildly aggressive food product and corrosion was not expected to occur at high rate for stainless steel in such a mild solution.

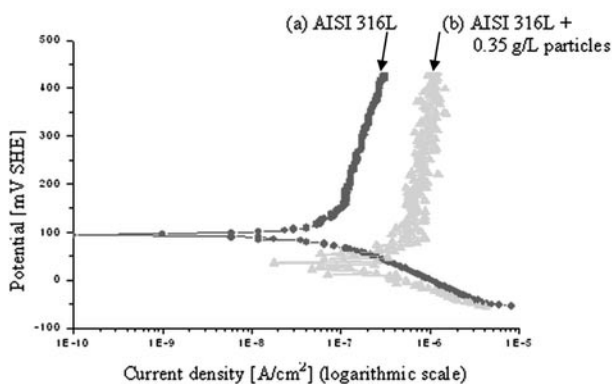


Figure 6—Polarization curve at a scan rate of 1 mV/sec for stainless steel AISI 316 L in 0.03 wt% chloride, 0.1M acetate buffer at pH 5.5 with (a) erosion 0.35 g/L, 250- μm alumina particles and (b) without erosion.

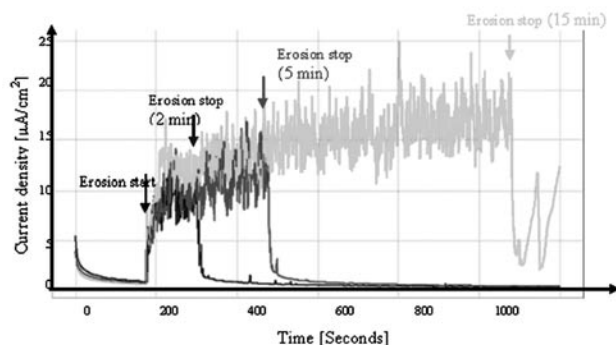


Figure 7—The resulting current at a fixed potential of $644 \text{ mV}_{\text{SHE}}$ has been monitored for untreated AISI 316 L. Three erosion time durations were studied: 2, 5 and 15 min. The solution was 0.05M sodium citrate/citric acid buffer at pH 4 with a NaCl concentration of 0.5 wt% and 0.5 g/L 250- μm alumina particles.

In a higher chloride-containing food simulation solution, the resulting current at a fixed potential of $644 \text{ mV}_{\text{SHE}}$ was monitored for three erosion time durations: 2, 5 and 15 min. The fixed potential of $644 \text{ mV}_{\text{SHE}}$ was in the passive region of stainless steel and in the anodic region of low temperature-nitrided stainless steel.

Figure 7 shows how the three curves are similar until erosion starts as well as during erosion. The fluctuations during erosion were a consequence of particle impacts. The current increase with erosion time was probably due to an area increase of the wear track. As erosion stopped, repassivation was seen, but after 15 min of erosion the surface seemed to be only slightly attacked by local corrosion, which explains the current scattering after erosion had stopped. The enhancement of metastable pitting of stainless steel in chloride solution has been documented previously¹⁴ and is believed to be due to exposure of fresh active sites during erosion.

The effect of low temperature nitriding

Potentiostatic monitoring of the open circuit potential during erosion-corrosion was performed to investigate the effect of low temperature nitriding of stainless steel. The curves in Fig. 8 show how the open circuit potential of untreated AISI 316 L decreased by approximately 250 mV as a consequence of erosion. The nitrided AISI 316 L decreased by 100 mV and maintained a level similar to untreated AISI 316 L without erosion. Further, the low temperature nitrided stainless steel had a higher open circuit potential than untreated stainless steel during erosion. This indicates that the passivating layer properties were affected by the low temperature nitriding process.

DLC and DLC-duplex

The topography of the specimens was generally similar to the one schematically shown in Fig. 9, by the use of a non-destructive laser measurement. The surface morphology indicates how the middle of the wear track degraded to a lesser extent than the outer circle of the wear track.

Fig. 10 shows how the three curves were similar until erosion started. After erosion stopped repassivation was not seen. The current measured was higher than that for untreated AISI 316 L as shown in Fig. 7.

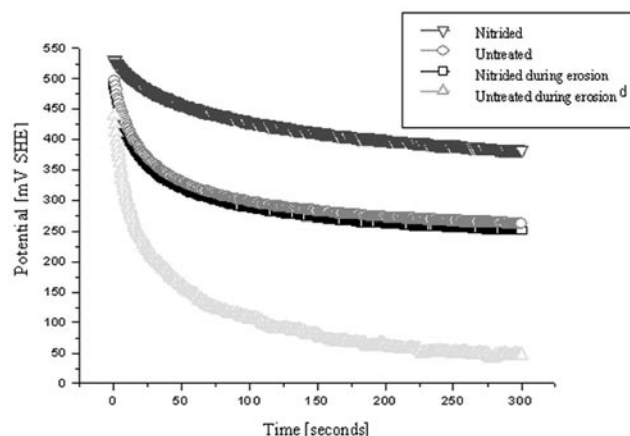


Figure 8—Open circuit potential for AISI 316 L and low temperature nitrided AISI 316 L in 0.03 wt% chloride, 0.1M acetate buffer at pH 5.5 with and without erosion of 0.35 g/L, 250- μm alumina particles.

The three curves shown in Fig. 11 are again similar until erosive conditions starts. After erosion repassivation was not seen. The currents measured for the 2 min and 5 min erosion duration were lower than for DLC, shown in Fig. 10. The specimen exposed to erosion for 15 min showed a drastic increase after approximately 700 sec indicating that the coating had been worn through or microcracks had been introduced in the DLC-duplex coating, because of the mechanical impact from the particles. After this the current increased to a value of $80 \mu\text{A}/\text{cm}^2$.

It is evident that the conventional nitrided layer had inferior corrosion resistance compared to the DLC thin film as indicated in Fig. 12, showing local corrosion of the conventional nitrided layer beneath the DLC thin film. A crack seems to have initiated at the edge of the DLC coating and propagated through the nitrided layer. This could be an effect of the preparation of the cross section.

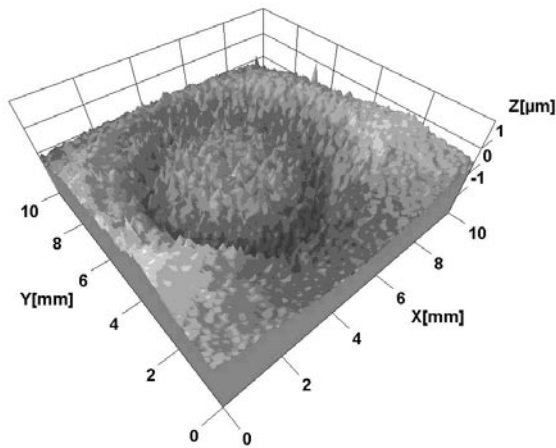


Figure 9—Surface topography made by nondestructive laser measurement of DLC-coated AISI 316 L after erosion-corrosion in 0.05M sodium citrate/citric acid buffer at pH 4 with a sodium chloride concentration of 0.5 wt% and 0.5 g/L 250- μm alumina particles.

Conclusion

Erosion-corrosion is a tribocorrosion process known to degrade materials at higher rates than expected due to a synergistic effect between wear and corrosion. Stainless steel is often used in the food industry for processing of food products which can become corrosive due to low pH, high salt content and high processing temperatures. Furthermore cleaning and sanitizing agents can be corrosive to process equipment used in the food industry. Unexpected material failure can occur if the stainless steel surface is exposed to erosive wear caused by abrasive particles combined with a corrosive solution.

In order to optimize the surface of stainless steel to withstand erosion-corrosion there is a need to determine the material degradation caused by erosion and corrosion respectively, as well as the combined effect. A setup, described in this paper, can be used for

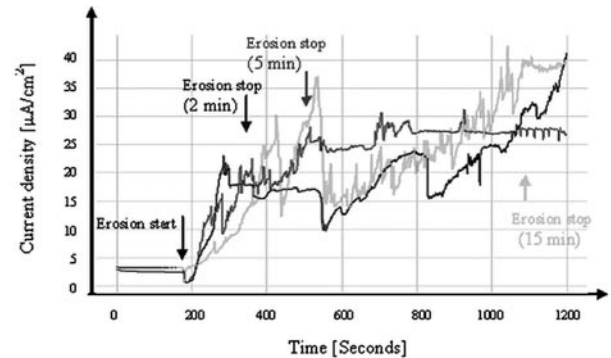


Figure 10—The resulting current of the DLC coating has been monitored at a fixed potential of $644 \text{ mV}_{\text{SHE}}$ for three erosion time durations: 2, 5 and 15 min in 0.05M sodium citrate/citric acid buffer at pH 4 with a sodium chloride concentration of 0.5 wt% and 0.5 g/L 250- μm alumina particles.

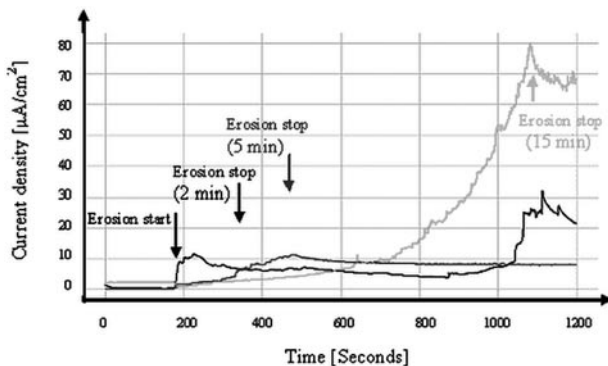


Figure 11—The resulting current of the DLC-duplex multilayer coating has been monitored at a fixed potential of $644 \text{ mV}_{\text{SHE}}$ for three erosion time durations: 2, 5 and 15 min in 0.05M sodium citrate/citric acid buffer at pH 4 with a sodium chloride concentration of 0.5 wt% and 0.5 g/L 250- μm alumina particles.

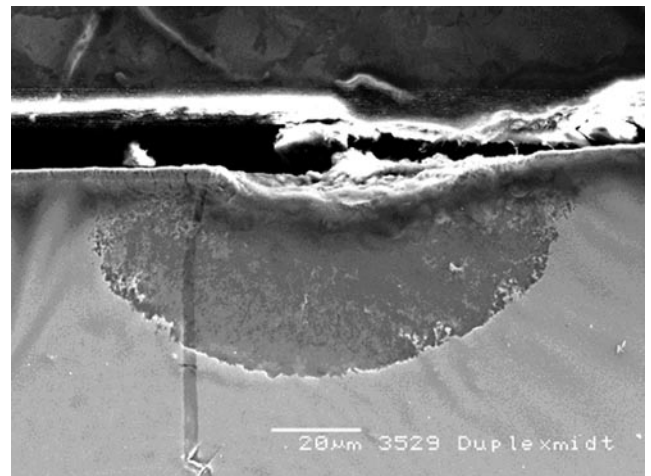


Figure 12—DLC-duplex after erosion-corrosion in 0.05M sodium citrate/citric acid buffer at pH 4 with a NaCl concentration of 0.5 wt%, showing under-corrosion of the conventional nitrided stainless steel substrate.

this purpose. The setup allows specimens to undergo erosion-corrosion while electrochemical measurements are performed online, in real time. The results can be used to optimize the surface properties, estimate life time of process equipment and evaluate the effect of environment composition, particle concentration, fluid velocity, etc. The following results have been obtained:

- Erosion with only 0.35 g/L alumina particles has shown a significant change in the corrosion resistance of stainless steel even in a mildly corrosive solution. A more distinct synergy effect between erosion and corrosion is likely to appear if the solution pH decreases and salt content increases, which can be the case for various food products like juices or other acidic products.
- Low temperature nitriding is a process for hardening the surface of stainless steel with expanded austenite without deterioration of the corrosion properties. Low temperature nitriding has been shown not only to decrease the wear rate as compared to untreated stainless steel, but also doing so without deteriorating the corrosion properties of stainless steel. The results show an increase of hardness for the expanded austenite phase to 1160 HV_{5g} and an improvement of resistance to localized corrosion.
- Thin film coatings have been characterized with respect to erosion-corrosion properties. Initially the properties improved for samples with deposited DLC films, until the thin film broke down and the corrosion rate increased, as compared to untreated stainless steel. This effect is more distinct in the case of DLC-duplex, where the sub-layer of the conventional high temperature nitrided layer showed poor resistance to local corrosion attacks. Repassivation was not seen for the DLC-coated samples, as was the case with untreated stainless steel. The high corrosion current values for the DLC-coated samples as compared to stainless steel were probably related to local corrosion.

Future work is ongoing to improve the corrosion resistance of such conventional multilayer coatings with a sub-layer of low temperature nitrided stainless steel. Such a coating is expected to resist local corrosion attacks if the top layer breaks down locally.

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About the Authors



Morten S. Jellesen is currently studying for a Ph.D. degree at the Department of Manufacturing Engineering and Management, at the Technical University of Denmark (DTU), Lyngby. He holds a M.Sc. degree in chemical engineering from DTU.

Mads K. Hansen is an Engineering Consultant at the Danish Technological Institute, Aarhus C, Denmark



Lisbeth R. Hilbert is an Associate Professor in the Department of Manufacturing Engineering and Management at the Technical University of Denmark, in Lyngby, Denmark.



Professor Per Møller received his Ph.D. in electroplating from the Technical University of Denmark (DTU) in 1982. He has been Head of the Center of Advanced Electroplating, which was a part of The Danish Material Development Program with participation by several industrial companies. He has been a participant in a large number of surface technology projects in the European Union. Several of them have had a close relationship to research and education. Dr. Møller is currently employed as Professor in Corrosion and Surface Technology at the Technical University of Denmark. He has been a member of the AESF Research Board for many years.

Appendix V:

Erosion-corrosion and corrosion properties of DLC coated gas-nitrided austenitic stainless steel

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Erosion-corrosion and corrosion properties of DLC coated gas-nitrided austenitic stainless steel

Morten S. Jellesen, Thomas Christiansen, Lisbeth Rischel Hilbert, Per Møller

*Technical University of Denmark
Department of Manufacturing Engineering and Management
Kemitorvet b.204, DK-2800 Kgs. Lyngby, Denmark*

Abstract

Corrosion and erosion-corrosion measurements were performed to study the effect of gaseous nitriding on AISI 316 L stainless steel. Low temperature nitriding was performed in $\text{NH}_3/\text{H}_2/\text{N}_2$ gas mixtures at 445°C resulting in the formation of a supersaturated solid solution of nitrogen in austenite known as expanded austenite. High temperature (equilibrium) nitriding was performed in H_2/N_2 gas mixtures at 1090°C resulting in a relative thick nitrogen diffusion zone with low nitrogen content. Multilayer coatings, consisting of diamond-like carbon deposited on expanded austenite layers were investigated together with nitrided and untreated stainless steel. For comparison purposes massive copper and titanium were also included in the investigation. Potentiodynamic measurements performed in a slightly aggressive food simulating solution showed that the anodic reactivity of the stainless steel was only slightly influenced by nitriding, whereas the hardness of the layer was significantly increased. Erosion-corrosion data suggested that the total material loss was significantly smaller for the low temperature nitrided multilayer coated specimens than for untreated stainless steel, when exposed to an elevated electrochemical potential during erosive impingement conditions.

Keywords: Erosion-corrosion, stainless steel, expanded austenite, DLC coatings.

1. Introduction

Stainless steel is used in the food industry for processing of products being potentially aggressive due to low pH, high salt content or high processing temperatures. Most often stainless steel is an adequate material solution, but unexpected material failure can occur if the surface is exposed to external influences as e.g. erosive wear caused by abrasive particles. Such erosive wear interacting with corrosion is termed erosion-corrosion and is known to degrade materials at higher rates than expected, because of a synergistic effect between wear and corrosion. Research work focusing on improving the erosion-corrosion resistance of austenitic stainless steel via advanced surface engineering technologies considering the combined corrosion and wear behaviour has been scarce [1]. Erosion-corrosion failures of stainless steel used in the food industry have been reported [2] and relatively simple surface modifications can be an optimal technological solution to solve such problems. This work describes the material degradation in a food product simulating solution, caused by erosion and corrosion as well as the combined effect. The effect of low and high temperature nitriding of AISI

316 L stainless steel was studied together with diamond-like carbon (DLC) coatings as an additional coating on low temperature nitrided stainless steel and compared to untreated AISI 316 L and bulk titanium and copper. Copper is a soft material and known to be susceptible to erosion-corrosion, whereas titanium is used under extreme erosion-corrosion conditions. The purpose of this work is to investigate whether adequate resistance against erosion-corrosion can be established by surface modification of stainless steel, instead of making components in expensive massive materials such as titanium.

Diamond-like carbon films are known to be chemically inert and show high wear resistance in both ambient air and aqueous environment [3]. DLC films are only a few μm thick and when coated on a soft substrate, such as stainless steel, the load bearing capacity is low; the substrate will deform plastically and the DLC film will fall off as flakes[4]. Previous results have shown that stand-alone DLC-coatings have improved erosion properties until the layer breaks down, which is followed by an increase in the corrosion rate as compared to untreated stainless steel [5].

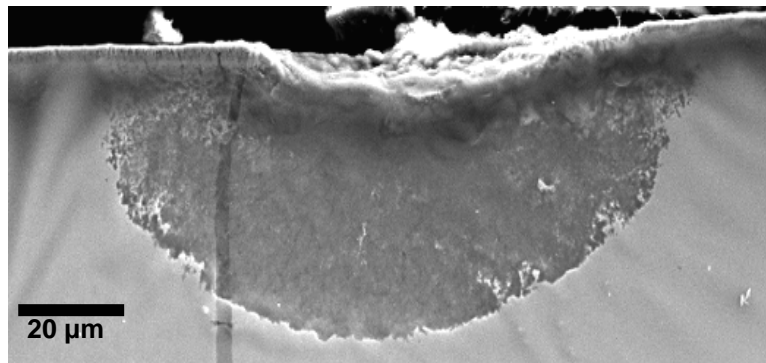


Fig. 1. DLC-duplex after erosion-corrosion in 0,5 wt.% NaCl, pH 4, showing under-corrosion of a conventionally nitrided stainless steel substrate [6].

The improvement of substrate hardness to support the top layer when exposed to mechanical impacts has previously been investigated [6]. A conventional multilayer coating used for wear applications was investigated and severe local corrosion was taking place of the conventionally¹ nitrided underlayer due to sensitization, as shown in fig. 1.

Therefore this work investigates how to improve the corrosion resistance of multilayer coatings with an under-layer of low temperature nitrided stainless steel. Two relative recent methods for improving the wear and corrosion resistance of stainless steel are investigated. Low temperature gaseous nitriding (LTN) is carried out at temperatures below approximately 450° in mixtures of $\text{NH}_3/\text{H}_2/\text{N}_2$ [7]. In this temperature regime the development of CrN is kinetically hindered and the corrosion resistance of the steel is unaltered or even improved [8]. The surface adjacent region is converted into so-called expanded austenite, which is a solid solution of high contents of interstitially dissolved nitrogen. The solubility of nitrogen in expanded austenite can be as high as 38 at.% N

¹ Conventional nitriding is carried in a temperature range where precipitation of CrN occurs in stainless steel, i.e. the corrosion properties are impaired.

[9], and the hardness of expanded austenite can reach 1200-1400 HV with a significant improvement of the wear resistance [7,8].

High temperature nitriding (HTN) is carried out in the temperature range 1050-1200°C in N₂ containing atmospheres [10,11]. In this temperature range Cr₂N is not formed and nitrogen goes into solid solution. The solubility of nitrogen is governed by the partial pressure of N₂, the alloy composition and the nitriding temperature. The high temperature equilibrium solubility of nitrogen is significantly lower than the nitrogen solubility in expanded austenite (paraequilibrium); typically a few atomic % N. The extent of the diffusion zone of nitrogen is much larger than for low temperature nitriding, although with a much lower nitrogen content. Diffusion depths of nitrogen of several millimetres are obtained within short times. Cooling from the nitriding temperature is a critical step as precipitation of Cr₂N occurs quite rapidly in the intermediate temperature range of 700-900°C. In order to maintain nitrogen in solid solution forced gas cooling is applied [8]. The hardness increase is not as high as for expanded austenite, the hardness for an austenitic stainless steel grade will normally not exceed 300HV after HTN. In many respects the HTN process can be considered as a surface engineering alternative to high nitrogen bearing (bulk) stainless steel.

2. Experimental

2.1 Materials and coatings

Specimens of stainless steels were machined to a final dimension of 15 × 15 mm with a wall thickness of 2 mm. The composition of the stainless steel type AISI 316 L used is given in Table 1.

Table 1 Composition of AISI 316 L stainless steel given in wt. %.

	<i>Fe</i>	<i>Cr</i>	<i>Ni</i>	<i>Mo</i>	<i>Mn</i>	<i>Si</i>	<i>C</i>	<i>P</i>	<i>S</i>	<i>V</i>
AISI 316 L	68,9	16,7	10,1	1,9	0,9	0,4	0,03	0,08	0,03	0,1

A Netzsch STA 449 thermobalance was used for nitriding. All specimens were polished to grit 4000 using SiC paper. The samples were Ni-activated before gaseous nitriding as described elsewhere [12].

LTN was carried out in a in a controlled atmosphere of 9 % N₂ / 55 % NH₃ / 36 % H₂. The temperature was 445°C and the nitriding time was 22 hours. After nitriding the catalytic Ni layer was removed with dilute HNO₃ and at the same time the samples were passivated.

HTN was carried out at 1090°C for 2 hours in a gas mixture consisting of 2% N₂ / 98% H₂. Cooling from the nitriding temperature was carried out at rate of more than 50 K/min.. Due to the relatively low cooling rate a low partial pressure of N₂ was applied which is associated with relatively low nitrogen content.

The applied DLC layer is an a:C-H (amorphous hydrogenated carbon) film layered on a low temperature nitrided (approximately 20 µm thickness) AISI 316 L substrate with an intermediate adhesion layer consisting of a functional gradient coating for improved adhesion. The coating is made by a sputtering process using a conventional chamber.

All untreated and nitrided stainless steel specimens were passivated in a 25 wt.% solution of nitric acid for 30 minutes at room temperature prior to corrosion and erosion-corrosion testing.

2.2 Characterisation

The chemical composition of AISI 316 L was analysed using optical emission spectroscopy (OES) as given in table 1. The microstructure and layer thicknesses were studied using a light optical microscope (LOM) after etching with Kahling's reagent for 20 seconds. The surface hardness was measured using a Futuretech FM 700 microhardness tester with a Vickers diamond applied directly to the surface and to the cross-section with a load of 5 g. A JEOL 5900 scanning electron microscope (SEM) from JEOL Ltd, Tokyo, Japan was operated under high vacuum conditions to study the effect of erosion-corrosion on the surface morphology.

2.3 Corrosion testing

Potentiodynamic measurements were performed using a Radiometer PGP201 potentiostat. A holder exposes an area of 1.64 cm² and contact is established via a gold plated spring on the backside of the specimen. Polarizations are performed using a standard calomel electrode (SCE) from -0,6 V to 1,2 V vs. SCE at a scan rate of 30 mV/min in 0,5 wt.% NaCl, 0,1M sodium citrate / citric acid buffer at pH 4,0. This electrolyte simulates a slightly aggressive food product.

2.4 Erosion-corrosion testing

The test setup used allows for corrosion control and monitoring during erosion. The test design has previously been described in details [6] and is similar to the impinging jet apparatus described elsewhere [13,14]. It consists of a working electrode (the test specimen), an auxiliary electrode (a titanium net) and a standard reference electrode (saturated calomel electrode) connected to the solution by salt-bridging. The three electrodes were connected to a Radiometer PGP 201 potentiostat. Specimens were machined to a final dimension of 15 × 15 × 2 mm, polished and possibly surface modified, then appropriately cleaned, dried and weighed before testing. Replicates of all tests were made. The specimens were placed in the same holder used for corrosion testing exposing an area of 1.64 cm². The particle concentration was estimated by filtering 2 l samples (3 replicates) and determining the weight after filtering dry for exactly 1 minute. The fixed parameters used for erosion-corrosion investigation are shown in Table 2.

Table 2 Erosion-corrosion parameters.

<i>Specimens</i>	<i>Particles</i>	<i>Solution</i>	<i>Proces parameters</i>
Untreated AISI 316 L LTN AISI 316 L LTN AISI 316 L DLC coated HTN AISI 316 L Ti Cu	Al ₂ O ₃ size 250 µm	0,5 wt.% NaCl in a 0,1 M Na ₃ C ₆ H ₅ O ₇ , C ₆ H ₈ O ₇ buffer at pH 4,0	6 l/min = 5,2 m/s 1,9 g Al ₂ O ₃ /l Impact angle = 90 degrees 4 mm distance from jet Erosion period= 38 min Temperature 22-23 °C

As described in ASTM standard G119 [15] the total material loss, T , can be considered as in the following equation, where W_0 is the material loss due to wear without corrosion, C_0 is the material loss due to corrosion without wear and S is the material loss due to the total synergism interacting between corrosion and wear.

$$T = W_0 + C_0 + S \quad (1)$$

The total synergism (S) is the sum of the increase of mechanical wear due to corrosion, S' , and the increase of corrosion due to mechanical wear, S'' .

$$S = S' + S'' \quad (2)$$

The synergy effect S' is assumed to be negligible in these experiments. Electrochemical measurements at constant potential approximately quantify mass loss caused by corrosion, since mass loss can be related to charge (and thus the measured current) as described by Faradays law. These two assumptions makes it possible to obtain all degradation contributions by potentiostatic monitoring of the current at a fixed potential value, which is less time consuming than performing several experiments as suggested in ASTM standard G119. The total material loss (T) of the specimens was estimated using a microbalance with a sensitivity of 0,01 mg. The material loss due to corrosion without erosion (C_0) was approximated from the anodic current monitored without erosion. The synergy effect causing an increase in corrosion, as a consequence of erosion (S''), is approximated to be proportional to the increase in anodic current during erosion.

3. Results

3.1 Characterisation

LOM investigations on a cross section of a low temperature nitrided specimen showed a low temperature nitrided zone of approximately 15 μm (fig. 2). All investigated specimens contained uniform homogenous layers without any cracks.

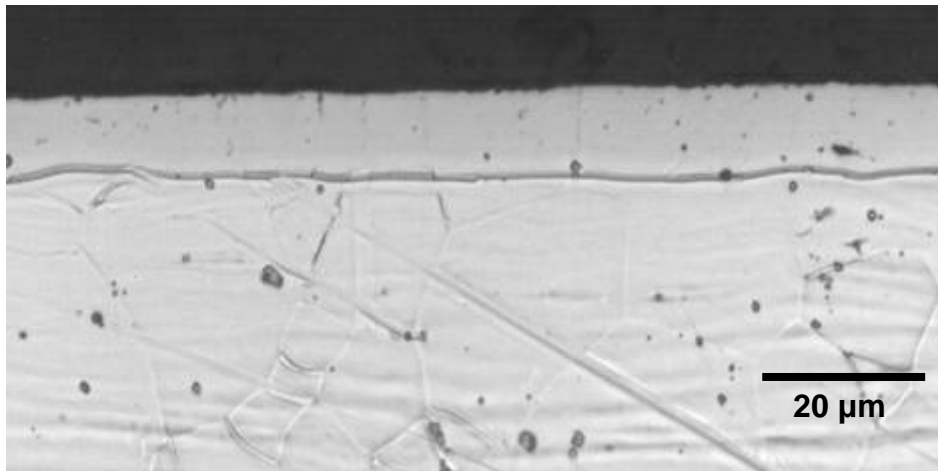


Fig. 2. Low temperature nitrided AISI 316 L.

The high temperature nitrided specimen was modified completely into nitrogen containing austenite. It has a significantly lower nitrogen content (> 2 at.%) than LTN resulting in lower hardness than a LTN layer, but still significantly higher than for untreated stainless steel.

Table 3 Microhardness measurements of the cross section of untreated, nitrided and DLC coated AISI 316 L, titanium and copper.

Material	Hardness HV0,005 Cross section	Hardness HV0,005
Untreated AISI 316 L	189	256
LTN AISI 316 L	1126	1162
HTN AISI 316 L	227	261
LTN AISI 316 L DLC coated	-	2336 *
Ti	155	243
Cu	86	107
Al ₂ O ₃ (abrasive particles)	-	1800-2000 [ref 16]

* This measurement was performed with 0,01 kg.

The hardness value given for DLC is from a measurement performed directly onto the specimen and is therefore to be considered a minimum value due, to the inevitable influence from the substrate.

3.2 Corrosion properties

The corrosion properties without influence of erosion were investigated by studying the anodic polarization behaviour as shown in the polarization curves (fig. 3).

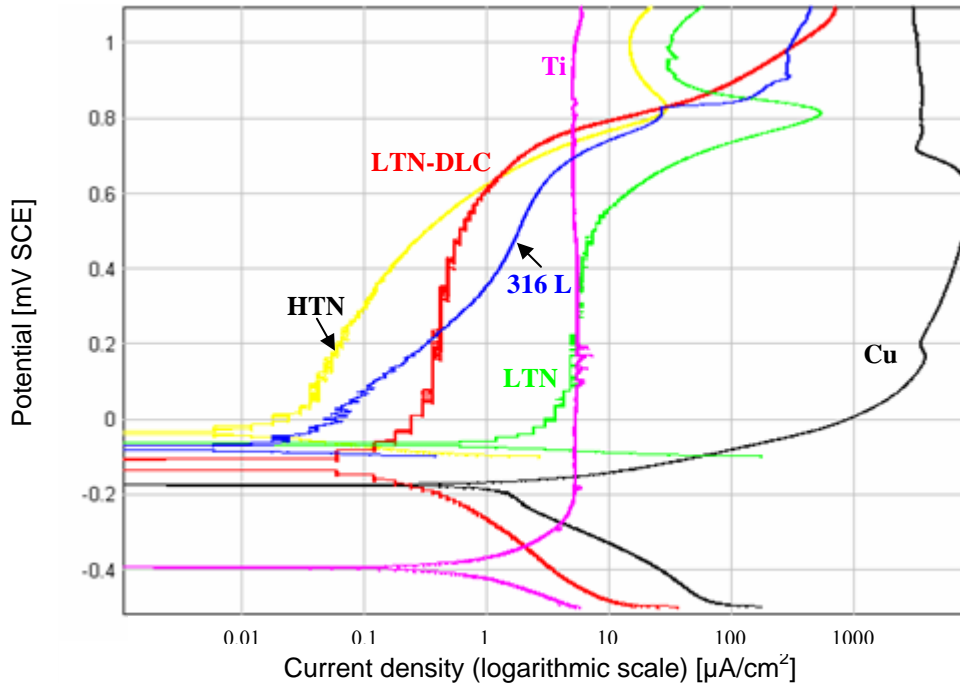


Fig. 3. Polarization curves at a scan rate of 30 mV/min in 0,5 wt.% NaCl, 0,1 M sodium citrate/citric acid buffer at pH 4,0.

The curves show how the corrosion potential for passivated nitrided and untreated stainless steel is similar and higher than unpassivated titanium and copper. The anodic current for the nitrided stainless steel in the passive region are slightly higher than for the untreated steel, but in the transpassive region the current is lower for the nitrided stainless steel. HTN shows the lowest passivation current, but it should be mentioned that this specimen was polished for 2 min before testing to remove a slight discolouration after the heat treatment. The polishing can affect the topography and thus minimize the surface area slightly.

3.3 Erosion-corrosion properties

The effect of erosion-corrosion was investigated by potentiostatic monitoring of the current at a fixed potential of 644 vs. standard hydrogen electrode (SHE). This value was chosen since it is the middle of the passive region of stainless steel.

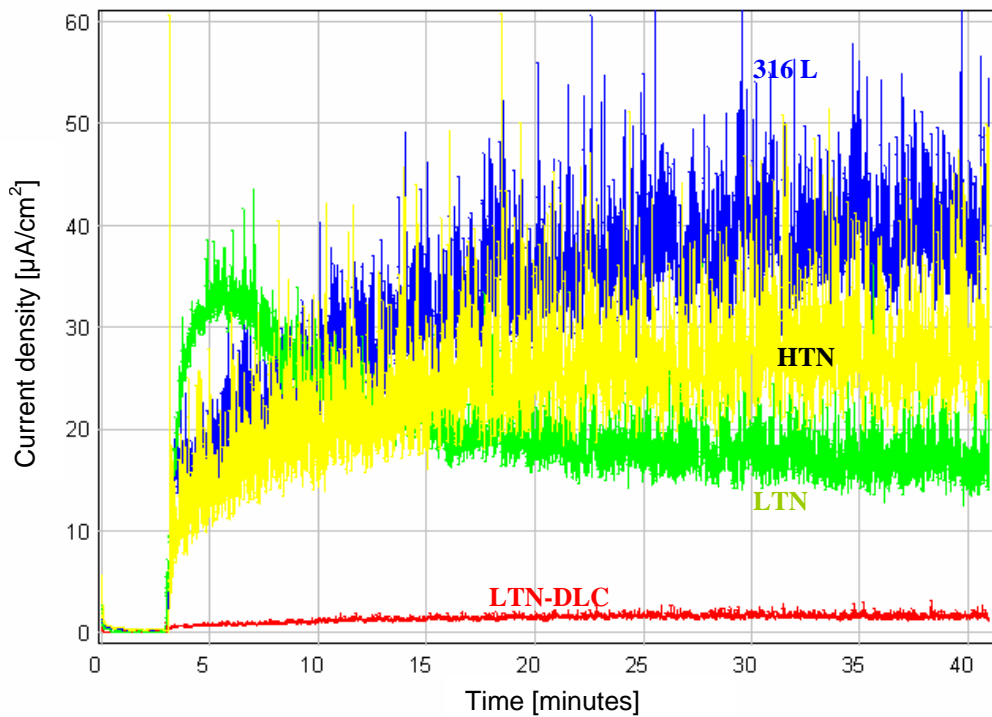


Fig. 4. Current density monitored in 0,5 wt.% NaCl for untreated, LTN, HTN, LTN and DLC coated AISI 316 L exposed to erosion from 3 to 41 minutes with 1,9 g/l Al_2O_3 at 644 mV SHE. Not shown are curves for Ti with similar current density values as HTN. The current density for Cu was in the range of several mA and neither shown.

Erosion starts after 3 minutes which can be seen as an abrupt increase in current for all specimens except LTN-DLC which remains at a low value throughout the experiment. The current values for 316 L and HTN increase throughout the experiment, whereas LTN has a maximum current value after 6 minutes where after the current value decreases. The area under the current density curves together with Faradays law gives the quantification of material degradation as shown in table 4.

Table 4 Material degradation in corrosion, wear and synergy parts.

<i>Material</i>	<i>Mass loss Total [mg]</i>	<i>Mass loss W+S' [mg]</i>	<i>Mass loss C +S'' [mg]</i>
<i>Untreated AISI 316 L</i>	<i>0,34</i>	<i>0,31</i>	<i>0,03</i>
<i>LTN AISI 316 L</i>	<i>0,20</i>	<i>0,18</i>	<i>0,02</i>
<i>HTN AISI 316 L</i>	<i>0,32</i>	<i>0,29</i>	<i>0,03</i>
<i>LTN AISI 316 L + DLC</i>	<i>0,09</i>	<i>0,08</i>	<i>>0,01</i>
<i>Cu</i>	<i>14,64</i>	<i>5,96</i>	<i>8,68</i>
<i>Ti</i>	<i>0,30</i>	<i>0,26</i>	<i>0,04</i>

For all specimens except copper the mass loss due to corrosion without the influence of erosion (C) is almost 0. The increase in corrosion due to erosion (S'') is clearly indicated in fig. 4, but the material loss due to corrosion is small when compared to the total mass loss, except for Cu.

The largest degradation part for all specimens except copper is wear (W) and the following examination in SEM also clearly indicates areas affected by plastic deformation.

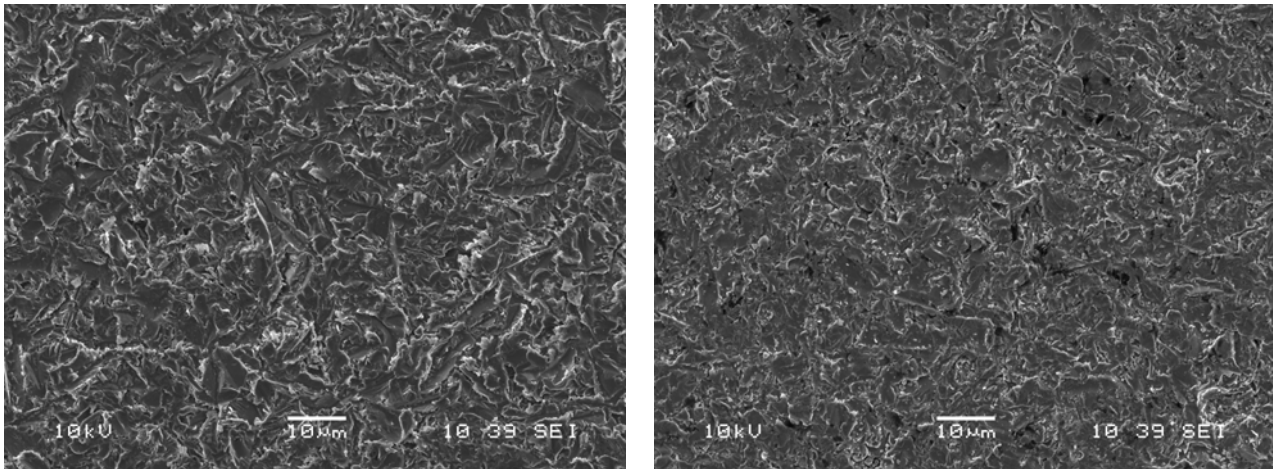


Fig. 5. Scanning electron microscopy surface analysis on AISI 316 L untreated (to the left) and LTN (to the right) after 38 min exposure to erosion–corrosion with 1,9 g/l Al_2O_3 at 644 mV SHE in 0,5 wt.% NaCl.

Fig. 5 clearly shows the effect of hardening the surface by nitriding. The untreated sample shows larger and deeper erosion impact craters than the nitrided sample that shows smaller and shallower depressions. None of the samples showed visible signs of corrosion.

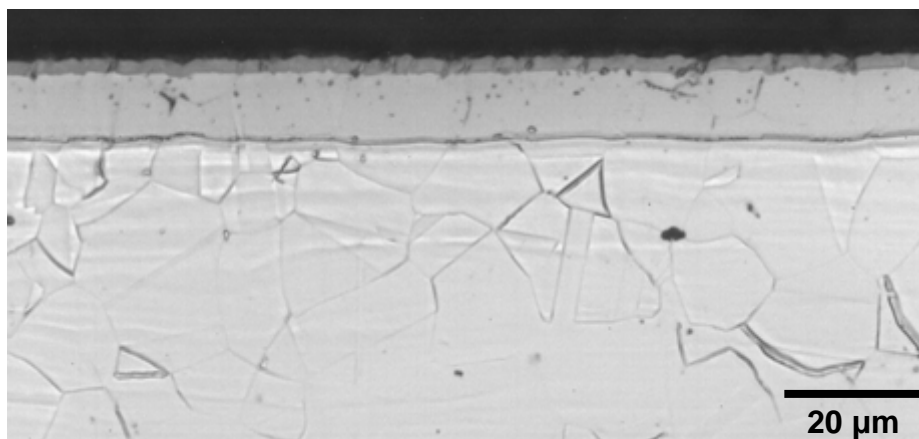


Fig. 6. Micrograph of eroded LTN-DLC.

The cross section of an eroded LTN-DLC specimen only show small impact effects on the surface.

4. Discussion

This work has described surface modifications of stainless steel and their resistance to corrosion and erosion-corrosion. To avoid nitride formation and sensitisation, nitriding at lower temperatures can be performed. Anodic polarisation curves indicate that the corrosion properties of AISI 316 L are slightly influenced by gaseous low temperature nitriding treatment. There has been some discussion in the literature regarding the effect of low temperature nitriding on the corrosion properties of stainless steel. In neutral chloride solutions, the corrosion resistance after low-temperature nitriding has been reported to be superior to untreated steels [17,18], whereas it at lower pH is reported to have a slightly negative effect on the corrosion resistance [10]. The enhanced corrosion reactivity of the low-temperature nitrided steel could be attributed to the presence of nitrides in the surface adjacent zone of the expanded austenite or to structural factors associated with relaxation of high compressive stresses in expanded austenite, i.e. cracking. Reported studies on the electrochemical behaviour of nitrided stainless steel have been based on plasma based technologies, which, due to the bombardment of the surface with ions, leads to a higher surface roughness and possible introduction of surface defects. This surface degradation may also affect the electrochemical properties of the plasmanitrided stainless steel negatively. Furthermore, the anodic behaviour of nitrided steels can also be affected by products of reduction or oxidation of nitrogen from steel, such as NH_4^+ , NO_2^- or NO_3^- [19].

Low temperature nitriding with subsequent DLC coating seems to improve the corrosion resistance as compared to untreated passivated AISI 316 L. The corrosion reactivity of high temperature nitrided stainless steel is lower than for untreated stainless steel. This improvement in electrochemical properties has to be ascribed to the presence of nitrogen in the HTN steel. Furthermore, as an inherent part of the HTN process, structural defects are removed and regions consisting of deformation martensite are converted into austenite. This may also have a positive effect on the electrochemical properties of the treated steel. However, it can not be excluded that the slight polishing

of the HTN samples, resulting in a slight topography change, could influence the results.

Nitriding was not conducted primarily to improve the corrosion resistance, but also to increase the wear resistance without impairing the corrosion resistance. This was investigated by erosion-corrosion investigations showing that the total material loss was significantly smaller for the low temperature nitrided and multilayer coated specimens when tested at an elevated electrochemical potential of 644 mV SHE during erosive impingement conditions. This value was not chosen arbitrarily, since it is representative for the passive region of stainless steel without exposure to erosion. There is a risk of failure of thin hard coatings after short test duration due to a high ratio of particle diameter to coating thickness [20]. It has been claimed that impact of very small particles is needed to detach the coating in small fragments in order to evaluate coating properties [21]. However, the erosion-corrosion testing performed in this work has proven to be a suitable tool for studies of crack initiation and propagation in thin hard coatings.

5. Conclusion

Gaseous low temperature nitriding of AISI 316 L stainless steel resulted in the formation of a supersaturated solid solution of nitrogen in austenite (expanded austenite). In 0.5 wt.% NaCl at pH 4, the anodic reactivity of the nitrided samples were comparable to untreated stainless steel but when exposed to erosion-corrosion the anodic corrosion current was significantly lower for the nitrided samples than for the untreated stainless steel. It has been shown that even minor amounts of nitrogen in austenitic stainless steel, as obtained by high temperature nitriding, have a beneficial effect on the corrosion behaviour.

This work has also shown that optimized resistance against erosion-corrosion can be accomplished using DLC depositing with proper underlayers to increase the load bearing capacity and avoid flaking of DLC. Gaseous low temperature nitriding has shown to be a promising underlayer for thin hard coatings used in tribocorrosive systems. Such underlayers are expected to resist local corrosion attacks if the top layer breaks down locally.

DLC-coatings are known for its beneficial properties under sliding wear situations, due to its lubricating effects and low coefficient of friction. Work is ongoing to establish the tribocorrosion behaviour during sliding wear and to investigate the appropriate thickness of nitrided underlayers.

Acknowledgement

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Appendix VI:

Nickel-containing coins: a health risk for nickel-sensitive individuals?

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ing vitiligo, acral areas respond very poorly to treatment. In a recent study analysing the effects of narrowband ultraviolet B on patients with nonsegmental vitiligo, it was reported that the patients showed marked response in 76.3% of facial lesions, 41.9% of truncal lesions and 37.6% of limb lesions. None of the patients achieved marked response in acral areas.⁴ This result is remarkable and has important implications. The repigmentation process in vitiligo after phototherapy involves reactivation of MCs located in the hair outer root sheath or from the contiguous pigmented skin from which the MCs migrate into the depigmented skin. Although the number of hair follicle units per unit area and the amount of epidermal MCs in the acral area may provide a partial explanation for this phenomenon, it is likely that other factors, such as certain dermal components of acral parts, may impede proper MC migration. This hypothesis, if proven correct, would explain the scarcity of reports on acral pigmented EP and lack of therapeutic response in acral vitiligo. Therefore, further investigations on the differences in dermal components, particularly the distribution of different extracellular matrix components that have been shown to be important in MC migration,⁵ among various anatomical regions, are indicated to elucidate further the pathomechanisms involved in these two seemingly different yet closely associated clinical observations.

*Department of Dermatology,
Kaohsiung Medical University Hospital,
Kaohsiung, Taiwan

†Department of Dermatology, College of Medicine,
Kaohsiung Medical University,
100 Shih Chuan 1st Road,
Kaohsiung, Taiwan

‡Faculty of Biomedical Laboratory Science,
Kaohsiung Medical University,
Kaohsiung, Taiwan

E-mail: d700086@kmu.edu.tw

C.-C.E. LAN*

H.-S. YU*†

C.-S. WU‡

G.-S. CHEN*†

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Conflicts of interest: none declared.

Nickel-containing coins: a health risk for nickel-sensitive individuals?

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SIR, There is an ongoing debate whether nickel-containing (releasing) coins may be a risk factor for allergic contact dermatitis on the hands. The introduction of the 1- and 2-euro coins has stimulated this debate. Migration studies and patch test studies using the euro coins seem to favour the existence of such a risk but the clinical experience, epidemiological studies and experimental exposure studies are not in favour of any significant risk for nickel-sensitive individuals to develop hand dermatitis after contact with nickel-releasing coins.

Nestle et al.¹ found a high nickel release from the euro coins when exposed to synthetic sweat using the EU reference test method for nickel release.² However, this method has been developed and standardized to control the EU nickel directive regulating nickel-releasing items designed to be in direct and prolonged contact with the skin, e.g. buttons.³ Occluded patch testing with pure nickel coins and euro coins has elicited a positive test in nickel-sensitive individuals.^{4,5}

As contact with coins is not a prolonged and direct contact but an intermittent frictional contact other assays are needed to understand the possible risk. Staton et al.⁶ have developed a finger immersion method to assess nickel exposure in different occupations and found only a moderately elevated nickel level in cashiers. In a well-controlled coin-handling experiment including nickel-sensitive individuals Zhai et al.⁷ did not find any signs of allergic contact dermatitis on the hands.

We have established an in vitro model combining the effects of corrosion and friction (termed tribocorrosion). The effect of combined corrosion and wear is not taken into account in existing standards.⁸ The tribocorrosion set-up was used to investigate nickel release into the surrounding sweat solution. The coin surface was exposed to 250 mL synthetic sweat² at a fixed potential of 500 mV standard hydrogen electrode (SHE) for 1 h, after which the sweat was analysed for nickel by using a Perkin Elmer atom absorption spectrophotometer model SIMAA 6000 (Perkin Elmer GmbH, Überlingen, Germany). Three replicates were made. The same procedure was repeated under tribocorrosive conditions: rubbing with a disc covered with washable leather, rotating at a fixed speed of 60 r.p.m. with an applied load of approximately 50 g cm⁻² (Fig. 1). The experiments lasted 1 h. The results of atom absorption spectrophotometric measurements in the corrosion and tribocorrosion experiments are shown in Table 1. The results show a distinct decrease in nickel release when the coin is exposed to rubbing. The SD is increased for the tribocorrosion experiment, which is to be expected. Both corrosion and tribocorrosion experiments were performed at a slightly elevated potential (500 mV SHE), which increases the corrosion rate compared with not imposing a potential. Therefore the values

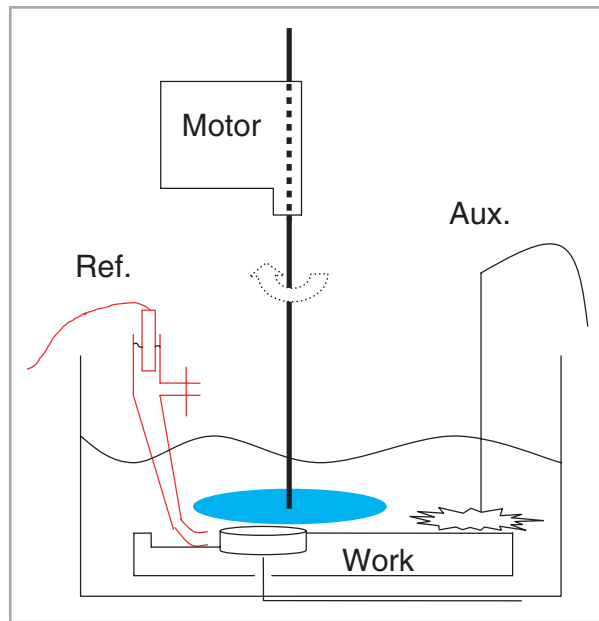


Fig. 1. Tribocorrosion set-up with motor, washable leather, auxiliary (Aux.) and reference electrode (Ref.). The mounted coin acts as the working electrode (Work).

Table 1 Nickel release from the euro alloy Cu75 Zn20 Ni5 (central alloy in the 2-euro coins determined after corrosion and tribocorrosion tests at an elevated potential of 500 mV standard hydrogen electrode (mean \pm SD of three replicates)

Test method	Nickel release ($\mu\text{g cm}^{-2} \text{ h}^{-1}$)
Corrosion	211 ± 3
Tribocorrosion	37 ± 16

are not a quantitative indicator of the nickel release caused by actual handling of coins, but clearly indicate how friction appears to decrease nickel release.

Scanning electron micrographs and surface analyses carried out by energy-dispersive X-ray spectroscopy after corrosion and tribocorrosion tests have indicated a change in surface morphology and composition. These investigations showed an increased content of carbon and chloride possibly from an insoluble chemical compound precipitated on the surface. As these indications are only qualitative, further investigations were made with X-ray photoelectron spectroscopy (XPS).

XPS has been used to analyse and quantitatively determine the Cu75 Zn20 Ni5 alloy surface composition after exposure to corrosion and tribocorrosion. The XPS analysis provides information on the elemental composition obtained from the top 10 nm of the substrate. It shows that the elemental composition does not correspond to the bulk stoichiometry and that Ni is detectable only in the surface oxide of the untreated surface. The remaining elements are mainly O, Cu and Zn, indicating that an oxide layer consisting of these elements has been formed.

After corrosion, the coin surface was enriched in Cu and Cl at the expense of Zn and O. This indicates that Zn (the less noble metal in the alloy) has corroded and that corrosion products containing Cl have been formed. After exposure to tribocorrosion, Cl-containing corrosion products were not detected at the outermost surface.

The results are in accordance with XPS surface analysis of euro coins taken from general circulation,⁹ where the presence of Cl, C and OH was indicated. However, that study also showed Ni enrichment compared with the bulk composition. In contrast, in the present study we found a decrease in Ni at the outermost surface after corrosion and tribocorrosion experiments.

A possible explanation for the decrease in nickel release under tribocorrosive conditions may be the change in transport kinetics. The washable leather may act as a diffusion barrier between the electrolyte and the coin surface. Another effect is the formation of a protective layer on the surface. Thermodynamic calculations resulting in a Pourbaix diagram¹⁰ of the composition of sweat indicate the formation of atacamite [$\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$] and malachite [$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$]. It is possible that a layer of atacamite and malachite is smeared on to the surface by the mechanical rubbing with washable leather during the wear test.

The present finding offers additional evidence on why handling of nickel-containing coins is not a significant problem for nickel-sensitized individuals. We also emphasize that the use of standard methods such as the EU reference method for nickel release should be restricted to the items (e.g. buttons) for which they have been developed and standardized. For other items such as coins and tools there needs to be developed specific standardized methods which take into account the effect of both corrosion and friction, simulating normal use.

Department of Manufacturing Engineering
and Management, Technical University
of Denmark, Kgs. Lyngby, Denmark
*Department of Dermatology,
Gentofte Hospital, University of Copenhagen,
Hellerup, Denmark
E-mail: mje@ipl.dtu.dk

M.S. JELLESEN
L.R. HILBERT
T. MENNÉ*
P. MØLLER

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Conflicts of interest: none declared.

New mutations of *KIT* gene in two Chinese patients with piebaldism

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Sir, Piebaldism is a rare autosomal dominant disorder of melanocyte development characterized by congenital and nonprogressive depigmentation of skin (leucoderma) and hair (poliosis). Its typical manifestations include a triangular white forelock and hyperpigmented macules on depigmented patches and normal skin. Depigmented patches are mainly found

on the scalp, forehead, trunk and limbs, and melanocytes are completely absent in the lesions.¹ Piebaldism has thus been thought to be a disease due to defective proliferation or migration of melanoblasts from the neural crest during early embryonic development.² Previous studies have revealed that piebaldism is caused by mutations of the *KIT* gene (also known as C-kit or CD117 gene) mapped on chromosome 4q12. This gene encodes for a KIT protein, a receptor for stem cell factor (SCF).³ Here we report two Chinese cases with piebaldism carrying two missense mutations in the *KIT* gene that have not previously been described.

Patient 1, a 10-month-old girl, and patient 2, a three-year-old boy, were both born with general static white patches on the scalp, forehead, trunk and limbs. A white forelock and hyperpigmented macules were also noted (Fig. 1). No family history of the disease or parental consanguinity were identified. Both patients were diagnosed as having severe sporadic piebaldism based on the typical clinical features. No facial dysmorphism, deafness, anaemia or heterochromic irises were found in either case.

Genomic DNA samples of the patients and their parents were prepared from their peripheral blood leucocytes after informed consent was obtained. All exons of the *KIT* gene and their flanking sequences were amplified and the PCR products were sequenced. We detected a nucleotide transversion of C1862A which results in Ala621Asp substitution in KIT protein in patient 1 and a transition mutation of T1784C which leads to Leu595Pro substitution in patient 2. None of their

Appendix VII:

Studies on Tribocorrosion Explain Low Nickel Release From Euro Coins

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Studies on Tribocorrosion Explain Low Nickel Release From Euro Coins

Morten S. Jellesen¹, Lisbeth Rischel Hilbert¹, Torkil Menné², Per Møller¹

¹ Department of Manufacturing Engineering and Management, Technical University of Denmark, Kemitorvet, IPL, DTU-Building 204, DK-2800 Kgs. Lyngby, Denmark.

² Department of Dermatology, Gentofte Hospital, University of Copenhagen, Niels Andersensvej 65, DK-2900 Hellerup, Denmark.

Abstract

Patch tests of 1- and 2-euro coins to the skin has shown to induce eczematous reactions, being more frequent and intense in comparison with those provoked by other coins. Handling experiments have however not indicated any risk of nickel release from euro coins. Nickel release is facilitated by corrosion of the coinage metal and is as such influenced by humidity, temperature and sweat composition. Furthermore it is known that combined corrosion and wear (tribocorrosion) can cause a synergy effect accelerating material degradation. The objective of this study is to investigate the effect of friction during handling, on the nickel release from euro coinage alloys. Electrochemical tests and tribocorrosion tests have been performed. The results surprisingly show a decrease in anodic current when combining corrosion and wear. A possible explanation for this finding is a change in transport kinetics and the formation of a passivating layer of atacamite $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ and malachite $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ smeared onto the surface by the mechanical rubbing with washable leather during the wear test.

Key words: Nickel release, corrosion, tribocorrosion, euro coins, nickel allergy.

Introduction

Nickel release from euro coins has previously been determined with a nickel release test¹ and it has been ascertained that the nickel release is 240-320 times higher than allowed under the EU Nickel

Directive.² Experiments with patch testing have shown strong erythematic reactions (irritated red skin) on nickel sensitized patients.^{2,3} Contrary to these laboratory results is the fact that handling experiments do not indicate any risk of nickel release from euro coins⁴ as well as the fact that no increase in nickel sensitizations has been detected in the general population referring for hand dermatitis (skin inflammation) since the euro became the official monetary unit of the European Union in January 2002.⁵

A recently reported method to quantify dermal nickel exposure is a finger immersion method, using Milli-Q water as a sufficient effective extractant.⁶ This method showed that the levels of nickel on the skin of cashiers' fingers were below the currently recognized nickel dermatitis occluded elicitation levels. Another technique for assessment of nickel exposure to skin is an acid wipe sampling technique. This method has been used for nickel determination after intense handling of coins for 30 minutes and levels of nickel found were ranging from 0,1-1,5 $\mu\text{g}/\text{cm}^2$.⁷

In this study we have examined the effect of friction from handling coins on metal release. European Standard 12472⁸ is the only standard regarding corrosion and wear and the standard is only relevant for materials with a protecting layer. Therefore it has been necessary to design a setup to study the effect of combined friction and wear on metal release. Combined friction and wear can be referred to as tribocorrosion. Tribocorrosion has been

defined as an irreversible transformation of a material caused by simultaneous physicochemical and mechanical surface interactions taking place in a tribological contact.⁹ As indicated in ASTM Standard G119¹⁰ several synergy effects are involved when combining mechanical and electrochemical phenomena.

The total material loss, T , can be considered as in the following equation, where W_0 is the material loss due to wear without corrosion, C_0 is the material loss due to corrosion without wear and S is the material loss due to the total synergism interacting between corrosion and wear.

$$T = W_0 + C_0 + S \quad (1)$$

Electrochemical measurements by the use of a potentiostat are a well-known method for determining metal degradation by corrosion. At a fixed potential the anodic current can be related to metal release via Faradays law.

$$m = n \cdot M = \frac{I \cdot t \cdot M}{z \cdot F} \quad (2)$$

The mass loss, m , is found from at determination of anodic current, I , time, t , the number of electrons, z , the molar mass, M and Faradays constant, F . This relationship indicates how an increase in anodic current can be directly related to an increase in metal release, if the anodic reaction leads to formation of dissolved ions. If the current is dominated by passive film formation, the released metal ion concentration will be significantly lower than foreseen from Eq. 2.

Studies On Tribocorrosion Explain Low Nickel Release From Euro Coins

Materials and Methods

Several circular blanks with the composition of alloys used for coinage have been studied with respect to nickel release. This work reports results obtained for a Cu75 Zn20 Ni5 circular blank and a newly struck 2-euro coin with the composition given in Table 1.

2-euro	Composition [wt.%]:
Inner pill	Cu75 Zn20 Ni5
External ring	Cu75 Ni25

Table 1 - The 2-euro composition.

As indicated in Table 1 the 2-euro consists of two alloys based on 75 wt.% Cu. The inner pill has a yellow colour, whereas the external ring is silver coloured. The inner pill contains an inner core of pure nickel not exposed to contact. A Perkin Elmer atom absorption spectrophotometer model 2380 has been used to quantify the release of nickel according to European Standard 18111.¹

Electrochemical and tribocorrosion tests have been performed at room temperature in a standard sweat solution with the composition: sodium chloride, 0,3 wt.%; lactic acid, 0,1 wt.% and urea, 0,1 wt.%. Ammonia solution was added to adjust the pH value to $6,50 \pm 0,10$. A standard three-electrode electrochemical setup was connected to a potentiostat. A titanium net served as a counter electrode and a standard calomel electrode (SCE, + 244 mV SHE) as a reference electrode. Tribocorrosion studies were performed using a setup previously described,¹² illustrated in Figure 1. The apparatus consists of a motor rotating a polymer disk with a radius of 10 cm. The disc is covered with washable leather and rotated at a fixed speed of 60 rpm. The applied load is approximately 50 g/cm^2 .

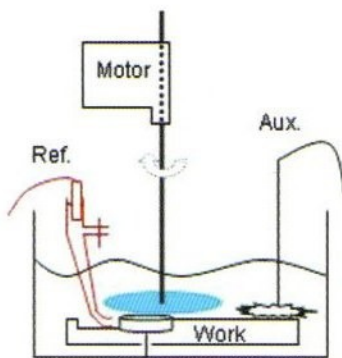


Figure 1: Tribocorrosion set up with motor, washable leather, auxiliary (Aux.) and reference electrode (Ref.) The mounted sample acts as the working electrode.

Test samples were made of 2-euro coins mounted in polypropylene with epoxy and connected as the working electrode. This sample design allowed the 2-euro to be used in a setup for corrosion as well as tribocorrosion investigations. The polarisation measurements were carried out at 22°C with a scan rate of 1 mV/sec . Washable leather was chosen as wear material, because it is comparable to the situation where human skin is in contact with the substrate. Prior to electrochemical investigations the 2-euro was washed with distilled water and dried. Circular blanks were polished with SiC grit 500, washed with distilled water and dried.

A Jeol scanning electron microscope (SEM) with X-ray microanalysis has been used to evaluate surfaces before and after exposure to tribocorrosive conditions. Energy dispersive analysis (EDS) is implemented in the SEM analysis and has therefore been used to provide qualitative analysis of the elemental composition.

X-ray photoelectron spectroscopy (XPS) was used to analyze and determine the Cu75 Zn20 Ni5 alloy surface composition after exposure to respectively corrosion and tribocorrosion performed at 500 mV SHE. Spectra were acquired with a Sage 100 (SPECS, Berlin, Germany) spectrometer equipped with a non-monochromated $\text{Mg}_{K\alpha}$ X-ray source operated at an effect of 275 W at a take-off angle of 90° . During data acquisition the base pressure was kept below 10^{-7} mbar . Atomic concentrations of each element were calculated by determining the relevant integral peak intensities using a linear type background. Satellite peaks have been excluded. The binding energies were referenced to the $\text{C } 1s^*$ peak (arising from inevitably environmental contamination) at 285 eV.

The tribocorrosion setup was used to investigate nickel release into the surrounding sweat solution by chronoamperometry. The coin surface was exposed to 250 ml sweat at a fixed potential of 500 mV SHE for one hour whereafter the sweat was analysed for nickel by atomic absorption spectroscopy. Three replicates were made. The same procedure was repeated under tribocorrosive conditions: rubbing with a disc covered with washable leather, rotating at a fixed speed of 60 rpm

with an applied load of approximately 50 g/cm^2 . Again three replicates were made.

Results

Results of nickel release tests (immersion test) performed according to European Standard 1811 are shown in Table 2. The values are indicating high nickel release for the inner pill as well as for the external ring of a 2-euro.

Samples	Nickel release [$0,5 \mu\text{g/cm}^2/\text{week}$]	Nickel release vs. limit value: [$0,5 \mu\text{g/cm}^2/\text{week}$]
Cu75 Ni25	98,9	198
Cu75 Zn20 Ni5	18,5	37

Table 2: Nickel release from alloys used in the 1 and 2-euro coins determined from atom absorption spectroscopy according to European Standard EN 1811.

The values are comparable to values presented elsewhere,^{2,13} indicating up to 200 fold more nickel release than the limit value regulated for European products intended to come into direct and prolonged contact with human skin.¹⁴

Figure 2 shows polarisation curves from experiments completed on the tribocorrosion setup with and without the influence of rubbing.

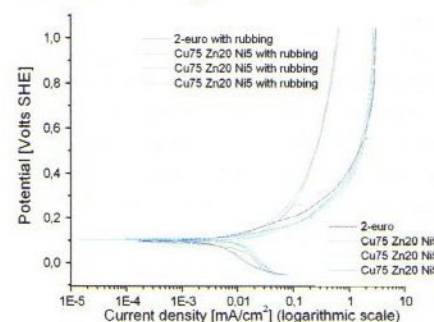


Figure 2: Polarisation curves of a 2-euro coin and three repetitions of blank circular discs made of Cu75 Zn20 Ni5 in synthetic sweat, with and without the influence of rubbing with washable leather. Above 0,2 volts SHE the current density decreases when the euro coin or coinage metal is exposed to wear.

The polarisation curves show a decrease in anodic current density when the euro coin or the blanks are exposed to wear. At 0,5 V SHE the current is decreased 5-6 times. This surprising phenomenon has shown to be the case for several coin alloys investigated; all with satisfactory reproducibility.¹¹

The decrease of anodic current is found in a potential range from 0,2 to 1 volts SHE.

Studies On Tribocorrosion Explain Low Nickel Release From Euro Coins

Spectrum wt. %	C	O	Cl	Ni	Cu	Zn
1	3,8	1,5	1,6	23,5	69,5	-
2	6,3	2,8	4,7	4,7	69,5	12,0



Surface analysis carried out by energy dispersive X-ray spectroscopy after tribocorrosion tests, states an increased content of chlorine Cl possibly from an insoluble chemical compound precipitated on the surface. Carbon is a light atom and the value is only legitimate as a trace element when found in energy dispersive spectrum analysis. Energy dispersive spectroscopy is only used as a method for qualitatively indicating the presence of species within a penetration depth of approximately 10 μm .

The SEM micrographs shown in Figure 4 illustrate the surface alteration after exposure to tribocorrosion during anodic polarization.

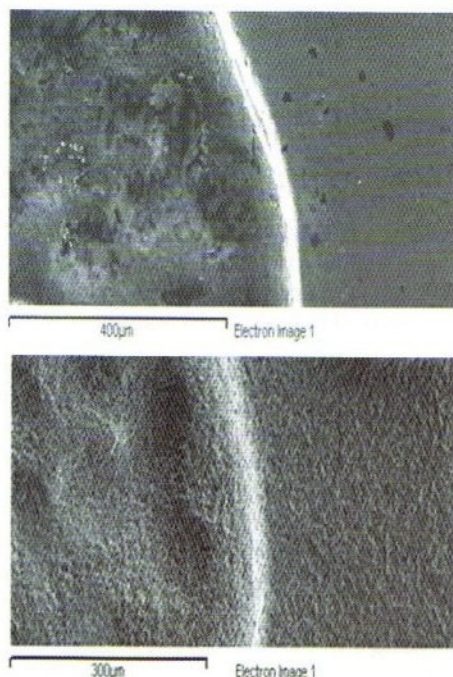


Figure 4: SEM micrographs of a 2-euro coin before tribocorrosion (above) and after tribocorrosion (beneath).

Figure 3: Picture and energy dispersive X-ray spectroscopy results of a 2-euro coin after exposure to tribocorrosion experiment.

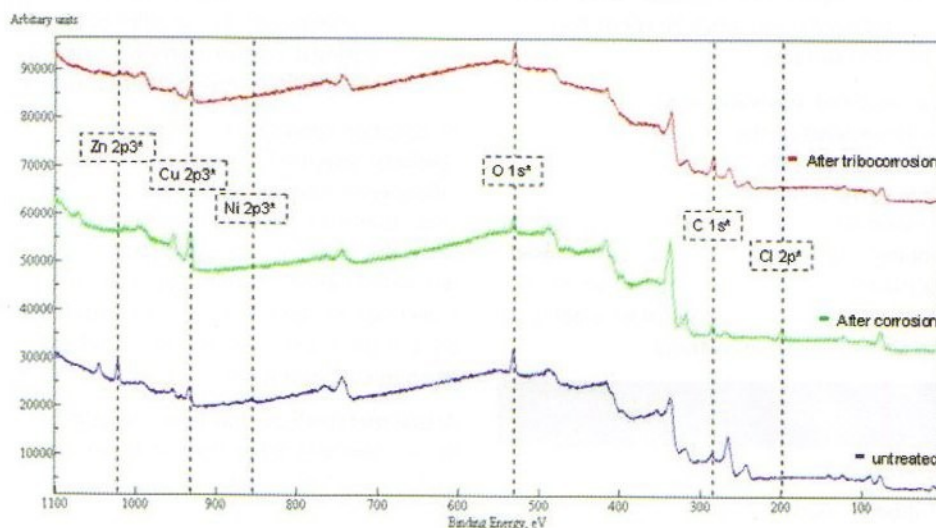


Figure 5: XPS survey scan of the Cu75 Zn20 Ni5 alloy indicating the relevant binding energy peaks of main elements present on the surface. The untreated coin has been polished with SiC grit 500, washed with distilled water and dried.

The coin exposed to corrosion has been polished likewise and then immersed in sweat at open circuit potential for 15 min and subsequently held at 500 mV SHE for 1 hour. The coin exposed to tribocorrosion has been exposed to wear during both the 15 min open circuit potential monitoring and subsequently chronoamperometry test at 500 mV SHE.

X-ray photoelectron spectroscopy (XPS) was used to analyse and quantitatively determine the Cu75 Zn20 Ni5 alloy surface composition after exposure to respectively corrosion and tribocorrosion. A survey scan is given in Figure 5.

At the given take-off angle the XPS analysis provides information of the elemental composition obtained from the top 10 nm of the substrate. The systematic error is estimated to be in the order of 5-10 at.%. Environmental contamination is to be expected and will inevitably cause a C peak.

The main points to be extracted from the quantitative analysis given in Table 3 of the

outermost surface of the Cu75 Zn20 Ni5 alloy are:

- For the untreated surface the elemental composition does not correspond to the bulk stoichiometry. Especially Ni is clearly absent in the surface oxide. Environmental contamination has caused a C composition of 34,4 at.%. The remaining elements are

mainly O, Cu and Zn indicating that an oxide layer consisting of these elements has been formed.

- The coin surface after corrosion has been enriched in Cu, C and Cl on the expense of Zn and O. This indicates that Zn (the less noble metal in the alloy) has corroded and corrosion products containing Cl have been formed.
- After exposure to tribocorrosion the surface contains a large amount of C together with O, Cu and Zn. Corrosion products containing chlorine has not been detected at the outermost surface.

Substrate	Cu	Ni	Zn	O	C	Cl
Untreated	7,4	0,6	11,1	46,4	34,4	-
After corrosion	17,2	-	-	25,8	42,2	14,8
After tribocorrosion	5,7	-	1,0	29,5	63,8	-

Table 3 - Atomic concentrations (at.%) of elements measured by XPS for the Cu75 Zn20 Ni5 alloy. Elements below detectable limit are marked by a straight line (-).

Studies On Tribocorrosion Explain Low Nickel Release From Euro Coins

• Only the untreated surface seem to contain Ni in a small amount. This is in accordance with the consideration that Ni is the noblest element in sweat compared to Cu and Zn. The results suggest that Ni remains in the bulk while Cu and Zn are available for oxide layer reactions. Apparently this also counts for the Cu75 Zn20 Ni5 alloy after exposure to corrosion and tribocorrosion, since Ni is not detected on these surfaces.

The results of atom absorption measurements of the corrosion and tribocorrosion experiments are shown in Table 4. The results show a distinct decrease in nickel release when the coin is exposed to rubbing. The standard deviation is increased for the tribocorrosion experiment which is to be expected. The release under rubbing is 5-6 times lower than without.

Test method	Nickel release [$\mu\text{g cm}^{-2} \text{h}^{-1}$]
Corrosion	211 +/- 3
Tribocorrosion	37 +/- 16

Table 4: Nickel release from the euro Cu75 Zn20 Ni5 alloy determined after corrosion and tribocorrosion test methods. Three replicates have been performed.

Both corrosion and tribocorrosion experiments have been performed at a slightly elevated potential (500 mV SHE) which increases the corrosion rate as compared to not imposing a potential. Therefore the values are not quantitatively indicating the nickel release in real use, but the values clearly show the influence of friction. The experiments lasted 1 hour and the values given in Table 4 are given pr. hour, whereas the values in Table 2 are pr. week.

Discussion

Nickel allergy is common and primarily a cause of direct and prolonged (defined by type of items as hours) contact with nickel releasing metal items as e.g. watches, costume jewellery and buttons.¹⁵ Regulation of nickel release by EU (2005) from such items has lead not only to a decrease in incidence of nickel allergy in young females, but also to a decrease in hand eczema, related to nickel allergy.^{16,17}

Results of the nickel release tests performed according to European Standard 1811 are indicating high nickel release for the inner pill as well as for the external ring of a 2-euro. The reason for the high level of nickel

release compared with the limit value is the highly unlikely situation that the coins are continuously exposed (immersed) to sweat for a week. Normal handling of coins is assumed to be of much less exposure time, and only exposure in short interval between dry conditions. There is also a difference in the surrounding environment between a coin freely exposed to sweat solution and that of handling coins in the palm of the hands, causing dissimilar transport kinetics of corrosion products formed at the surface.

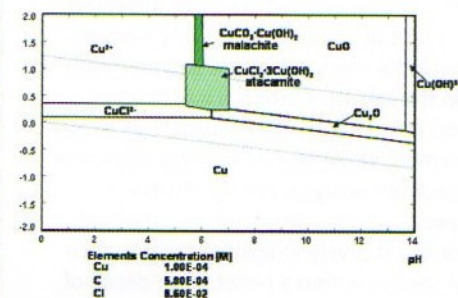
Polarisation curves of a 2-euro coin in synthetic sweat with and without the influence of rubbing with washable leather show that the current density decreases when the euro coin is exposed to wear. This decrease in anodic current can be related to a decrease in metal release as indicated by Eq. 2. If this is the case the synergy effect given in Eq.1 is negative.

Actual metal release has been investigated in corrosion and tribocorrosion experiments performed at an elevated potential. The higher potential is accelerating the mechanism, and therefore the values are not indicating the nickel release in real use. However, the values clearly show the positive influence of friction on reducing metal release. This is a surprising finding since most often total material loss will increase when combining corrosion and wear. The total synergism, as indicated in Eq. 1, interacting between corrosion and wear is negative in this case. So both the electrochemical data and the actual metal release give a negative synergism, which should be explained. The negative synergism could be related to changed transport kinetics, i.e. the washable leather acting as a diffusion barrier between the electrolyte and the coin surface or an effect of the formation of a protective layer on the surface.

Scanning electron micrographs and surface analyses carried out by energy dispersive X-ray spectroscopy after corrosion and tribocorrosion tests have indicated a change in surface morphology and composition. Since these indications are only qualitative further investigations were made with X-ray photoelectron spectroscopy. These investigations state an increased content of carbon and chlorine possibly from an insoluble chemical compound precipitated on the surface.

A possible explanation for these results is reduced transport kinetics during wear and the formation and precipitation of a passivating layer. Thermodynamic calculations, illustrated in Figure 6, verify the thermodynamically stability of atacamite $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ and malachite $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$. It is possible that a layer of atacamite and malachite are being smeared onto the surface by the mechanical rubbing with washable leather during the wear test.

Figure 6: The Pourbaix diagram¹⁸ calculated for artificial sweat and based upon thermodynamic considerations for a Cu-C-Cl-H₂O - System at 25 °C with a Cu concentration of $1,00 \cdot 10^{-4} \text{M}$. The diagram shows the possible formation of atacamite and malachite within the pH region of sweat.



The Pourbaix diagram Figure 6 shows that to minerals found in nature, atacamite $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ and malachite $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$, are possible species to be formed at the coin surface under influence of sweat at pH 6,5 above a potential of 0,2 volts SHE. Since the potential in the experiments is fixed at 0,5 mV SHE this is likely to occur.

It is expected that malachite and atacamite are species that can adhere to the surface under the influence of the rubbing motion during the wear test or from physically handling of the coins. The smearing properties of malachite and atacamite on a surface are well known from the paint industry, where the mineral has been used for centuries as a green pigment for paint.

The presence of malachite and atacamite is in accordance with X-ray photoelectron spectroscopy surface analysis of euro coins taken from general circulation, where the presence of chloride, carbon and hydroxide is indicated. In addition to the sheilding effect of the washable leather during tribocorrosion it is possible that the formation and precipitation of malachite and atacamite can form a protective layer

Studies On Tribocorrosion Explain Low Nickel Release From Euro Coins

on the surface and thereby hinder corrosion and thereby nickel release.

Conclusion

Using a test setup simulating friction of handling we have found that nickel release is lower when euro coins are exposed to combined corrosion and wear as compared to exposure only to corrosion. Experimental and clinical evidence do not support that neither the traditional nickel coins (75 % Cu and 25% Ni) nor the new 1 and 2-euro coins are significant risk factors for hand eczema related to nickel allergy. The identification of reduced transport kinetics during wear and the formation of an adhering protective layer smeared on top of euro coins, developed during an experiment simulating normal use, can explain the safety of nickel for this application.

A tribocorrosion test setup as described in this work provides the possibility for determining the influence of parameters e.g. handling time and frequency, handling pressure, sweat composition on nickel release without the risk of causing eczema to subjects. The setup also allows for a various number of nickel containing alloys and plated nickel/nickel alloys to be investigated as well as other metallic materials that might cause allergic reactions by handling.

Acknowledgements

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Appendix VIII:

The electrochemical deposition of tin-nickel alloys and the corrosion properties of the coating

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The Electrochemical Deposition of Tin-Nickel Alloys and the Corrosion Properties of the Coating

by Morten S. Jellesen* & Per Møller

The electrodeposition of tin/nickel (65/35 wt%) is a unique coating process because of the deposition of an intermetallic phase of nickel and tin, which cannot be formed by any pyrometallurgical process. From thermodynamic calculations it can be shown that intermetallic phases can be formed through electrodeposition. The alloy has unique corrosion properties and exhibits surface passivation like stainless steel. The coating is decorative and non-allergic to the skin, can replace decorative nickel and nickel-chromium coatings in many cases and decreases the risk for allergic contact dermatitis. A number of electrochemical tests, including polarization curves, chronoamperometric studies and tribocorrosion tests have been performed to show the consequence of replacing nickel coatings with tin/nickel coatings.

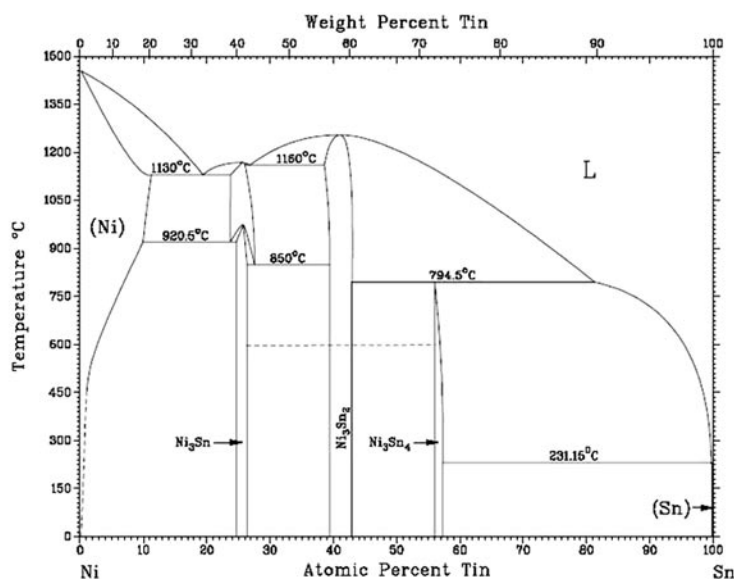


Figure 1—NiSn phase diagram.²

More than 50 years ago, Parkinson¹ published details describing a process to electroplate a deposit of nickel and tin with the composition of approximately 65/35 wt% (1:1 atom ratio) referred to as NiSn. This intermetallic phase of nickel and tin cannot be formed by any pyrometallurgical process and is not to be found in the phase diagram shown in Fig. 1.²

Nuts & Bolts: What This Paper Means to You

The electroplating of tin/nickel (65/35 wt%) is unique because the deposit structure cannot be formed by any thermal metallurgical process. It also has unique corrosion properties and exhibits surface passivation like stainless steel. With recent concerns about nickel allergies, this decorative finish is non-allergic to the skin, decreases the risk for allergic contact dermatitis and can replace decorative nickel and nickel-chromium coatings in many cases.

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* Corresponding author:
Morten S. Jellesen
The Technical University of Denmark
Department of Manufacturing Engineering and Management
Materials and Process Technology
Building 204, 2800 Kgs. Lyngby, Denmark
E-mail: mje@ipl.dtu.dk

Early descriptions explained the NiSn phase as an extension of the composition range of the equilibrium phase Ni_3Sn_2 . This extension was explained by more favored nucleation kinetics at the deposition temperature and the resistance of this deposit to transformation at low temperature.³ Later the structure of an equiatomic NiSn deposit was interpreted by C.C. Lo,⁴ who proposed that the electrodeposited tin-nickel alloy consisted of Ni_3Sn_2 within each grain and extra tin atoms segregated on the grain boundary.

It is known that the NiSn phase will reveal its metastable character when heated, as, above 350°C (662°F), it decomposes into the two stable equilibrium phases Ni_3Sn_2 and Ni_3Sn_4 .^{3,5,6}

In the late 1970s, a study was made into how the NiSn surface was protected from corrosion by a passive film which could be removed by mechanical wear.⁷ The authors found that if the substrate was exposed by wear-through or by brittle fracture of the NiSn, the corrosion resistance was determined by the substrate. It was also stated that freshly fractured edges of NiSn were severely corroded, while original NiSn surfaces and fractured edges exposed to air for three months were unaffected.

The effects of chloride, bromide or iodide ions on the passivity of NiSn alloys have also been studied.⁸ That work showed that the passive state of the NiSn alloy was not affected by halide ions up to the higher concentrations examined. In alkaline solutions containing chloride ions, the passivity of the NiSn alloy was far superior to that of both tin and nickel. Another study of the corrosion behavior indicated that a conversion of the metastable NiSn alloy did not degrade the corrosion stability of the deposit provided it remained coherent.⁹

In a 1987 study,¹⁰ it was stated that the NiSn alloy did not (or at least to a lesser extent) cause allergic reactions on nickel sensitive persons, while 9 out of 14 nickel-containing alloys caused medium to severe degrees of allergic reactions on nickel sensitive persons. The study also showed a reasonable correlation between *in-vivo* testing and electrochemical testing, except for Inconel® (77% Ni, 8% Fe, 15% Cr) which showed high reactivity when tested *in-vivo*. This is accounted for by the greater stability of the protective oxide layer during electrochemical tests than during the *in-vivo* tests.

The oxide layer of NiSn has been studied using electron spectroscopy for chemical analysis (ESCA), estimating a thickness of 30 Å.² Other investigations, using low energy ion-scattering spectroscopy to determine the surface composition showed a clearly evident absence of Ni in the surface region (5 to 10 Å).¹¹ The results confirmed earlier Auger electron spectroscopy studies and were consistent with the idea that since tin is more readily oxidized than nickel, a tin oxide will form on the surface. Furthermore it was pointed out that a tin-rich surface may also form in the absence of oxygen due to differences in surface-free energies.

Nickel release can be evaluated according to European Standard EN 1811.¹² The method in this standard is to expose the substrate to synthetic sweat solution for a week. The nickel released is

determined by atomic absorption spectroscopy and is related to the surface area. The upper limit for nickel release, according to a 2000 Danish regulation, is 0.5 $\mu\text{g}/\text{cm}^2$ (0.007 lb/in²) per week. If the substrate has a surface layer, a suggested standard test is European Standard EN 12472,¹³ where the substrate is exposed to simulated wear prior to the EN 1811 test.

Experimental

NiSn has been deposited on copper alloys and solid nickel from a commercial galvanic bath with the composition: tin, 25 g/L (3.3 oz/gal); nickel, 65 g/L (8.7 oz/gal) and fluoride, 33 g/L (4.4 oz/gal). The bath was operated at a pH of 4.5 and a temperature of 70°C (158°F). Nickel was used as the anode. A cathode current density of 2.0 A/dm² (18.6 A/ft²) was applied. Further details concerning the deposition and thicknesses for various service conditions are described in ASTM Standard B605.¹⁴

The solution used for electrochemical testing was a synthetic sweat solution prepared according to European Standard EN 1811.¹² The solution composition was: sodium chloride, 0.3 wt%; lactic acid, 0.1 wt% and urea, 0.1 wt%. Ammonia solution (1%) was added to adjust the pH value to 6.50 ± 0.10.

X-ray diffraction patterns of the as-electrodeposited NiSn layer are shown in Fig. 2. Because of crystallographic texture effects, the scan was repeated at different ψ -tilt angles to obtain as many identifiable {hkl} line profiles as possible. The various diffractograms are shown with offset on the intensity axis. A total of 11 peaks were identified as being consistent with the crystal structure proposed for Ni_3Sn_2 . The *a* and *c* lattice parameters determined from the peak positions of the {HK2} and {10L} line profiles, respectively were *a* = 4.173 Å and *c* = 5.123 Å and resembled those found by Lo⁴ for electroplated NiSn with lattice parameters *a* = 4.15 Å and *c* = 5.10 Å (See the peak positions indicated in Table 1.). A few diffraction peaks could not be identified as Ni_3Sn_2 , indicated by a question mark in Fig. 2. The results indicated that as-electrodeposited NiSn mainly consisted of Ni_3Sn_2 with a hexagonal structure of the NiAs type.

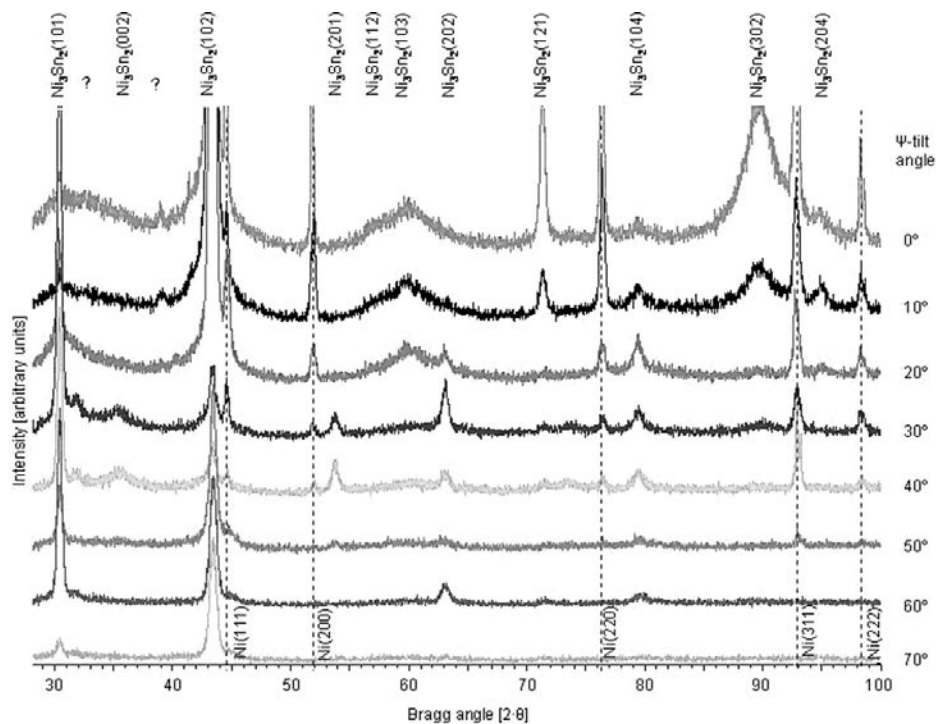


Figure 2—X-ray diffraction patterns (CuK α) of electrodeposited NiSn on a nickel substrate. The scan is repeated for eight different tilt angles. Nickel peaks from the substrate are marked with dotted lines.

Table 1
Observed peak positions consistent with structure proposed for Ni₃Sn₂

{hkl}	101	002	102	201	112	103	202	121	104	302	204
2θ	30.31	35.35	43.23	53.67	57.30	59.70	63.09	71.27	79.42	90.10	95.00

The composition of the alloy was determined using energy dispersive spectroscopy to be Sn/Ni 68.4/31.6 wt%, or 51.7/48.3 at% (Fig. 3).

Electrochemical tests

Electrochemical tests were all performed at room temperature in synthetic sweat solution with the composition described earlier. A standard three-electrode electrochemical setup was connected to a potentiostat.** A wound platinum wire served as a counter electrode and a standard calomel electrode (SCE, +244 mV_{SHE}) as a reference electrode. The sample to be investigated was the working electrode. Samples were made of 2.0-mm thick (ø25 mm) [0.8-in. thick (ø1.0 in.)] discs mounted in polypropylene with epoxy. This allowed the working electrode to be used in a setup for tribocorrosion investigations.

Corrosion studies

Corrosion studies were performed with pure nickel, austenitic stainless steel AISI 304 and copper alloys plated with NiSn. Samples were polished to a 1000 grit finish, except for the NiSn deposit, which was unpolished after plating. The copper alloy substrates were already polished to a 1000 grit finish. Galvanic couplings between NiSn and brass (63% Cu, 37% Zn), ASTM A284 steel, AISI 304 and zinc were also investigated using zero resistance amperometry.

As shown in Fig. 4, the passivation behavior of NiSn exceeded that of AISI 304 when polarized from -150 mV_{SHE} to 1050 mV_{SHE} at a scan rate of 0.5 mV/sec. It is important to note that the deposit must be free of pores. A simple test to evaluate the existence of pores involved immersion of the plated substrate in concentrated nitric acid. Pores will reveal themselves after a few minutes through excessive bubbling.

Figure 4(a) shows the repeatability of polarization curves of NiSn

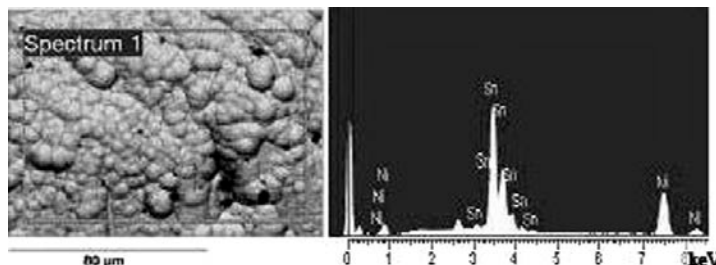


Figure 3—Scanning electron micrograph and energy dispersive spectroscopy analysis of NiSn electrodeposited on copper alloy.

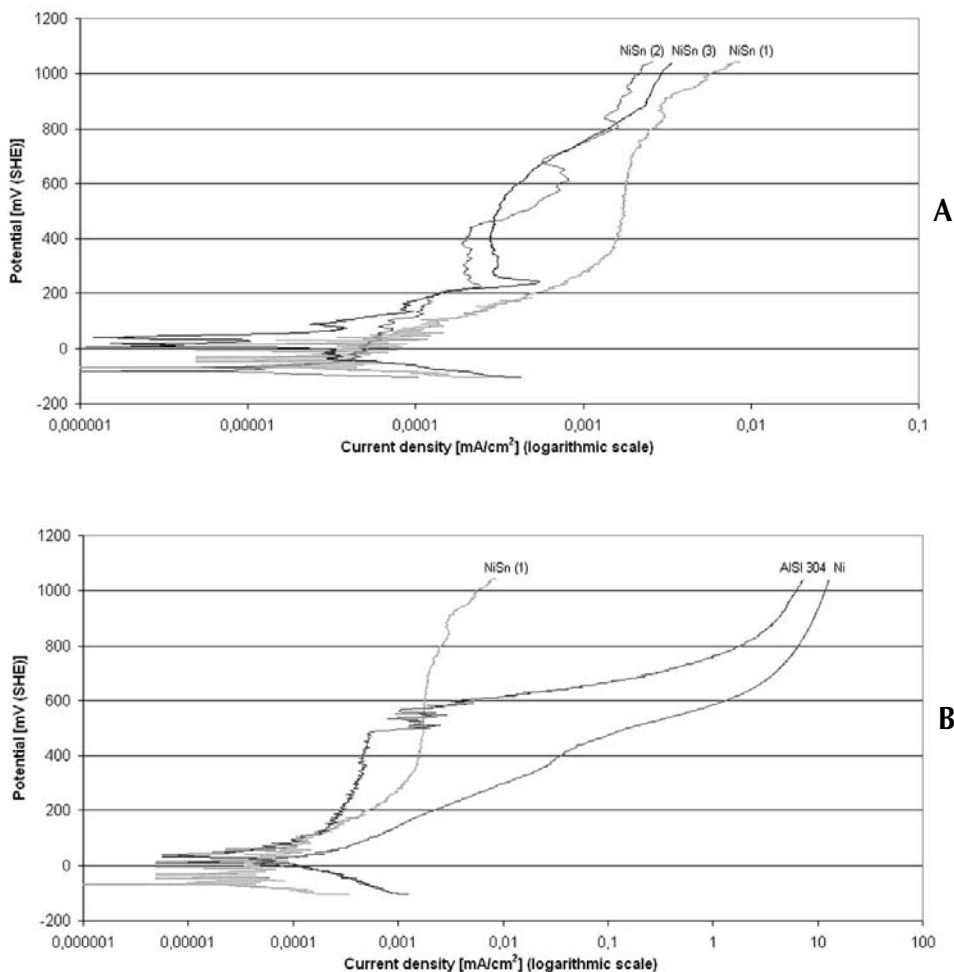


Figure 4—(a) Polarization curves of electrodeposited NiSn completed three times in synthetic sweat at a scan rate of 0.5 mV/sec; (b) polarization curves of electrodeposited NiSn, nickel and AISI 304 in synthetic sweat measured at a scan rate of 0.5 mV/sec.

** VoltaLab® PGZ 301 potentiostat, Radiometer Analytical, Lyon, France.

and how the deposit decreased its passive current after the first scan, suggesting a passivation after this initial scan. The curves of the second and third scans were similar. Figure 4(b) shows that the current density of the passive layer on AISI 304 and NiSn was comparable. However, the pitting potential of AISI 304 was approximately $520 \text{ mV}_{\text{SHE}}$, whereas the pitting potential for NiSn was still not reached at $1000 \text{ mV}_{\text{SHE}}$.

Galvanic couplings between NiSn, brass (63% Cu, 37% Zn), ASTM A284 steel, AISI 304 and zinc were carried out in synthetic sweat solution for comparison. Another environment where galvanic couplings could occur is drinking water where galvanic coupling between brass, steel and NiSn could be found in water pipe assemblies.

The increase in corrosion rate for the anodic part in various galvanic couplings is shown in Table 2. The data shows that when NiSn was coupled with zinc there was a risk of excessive degradation of zinc as it is the less noble part. Galvanic couplings between NiSn and brass (63% Cu, 37% Zn), ASTM A284 steel and AISI 304 did not seem to affect the corrosion rate excessively. NiSn did not degrade excessively in any of the investigated couplings since it acted as the cathode.

Tribocorrosion studies

Tribocorrosion studies were performed using the setup illustrated in Fig. 5. The apparatus consisted of a motor that rotated a polymer disk with a radius of 10 cm (3.9 in.). The disk was covered with synthetic washable leather. The motor rotated at a fixed speed of 150 rpm and the applied load was approximately 2.0 kg (4.4 lb.).

Washable leather was chosen as the wearing material, because it was comparable to the situation where human skin is in contact with the substrate. Electrochemical measurements could be made with the three-electrode setup, allowing potential and chronoamperometric studies of the substrate to be made with and without the influence of wear.

Prior to the tribocorrosion tests, the samples were briefly immersed in the solution until a steady open circuit potential was reached. The monitoring of the open circuit potential continued and after 10 min, the rotation of the washable leather was started. An abrupt decrease of the open circuit potential was observed (Fig. 6). When the motor was stopped (after 20 min), the open circuit potential increased, indicating a re-establishment of a passive film on the NiSn and stainless steel. Based on the open circuit potential monitoring, nickel seemed to be the metal least affected by wear.

In the chronoamperometric studies, a constant potential with respect to the reference electrode was applied and the anodic current was measured. The results are shown in Fig. 7. The constant potentials applied were $220 \text{ mV}_{\text{SHE}}$ for NiSn, $95 \text{ mV}_{\text{SHE}}$ for stainless steel and $100 \text{ mV}_{\text{SHE}}$ for nickel. It is important to note that the current densities were measured at different applied potentials for each sample. The potentials were fixed at approximately 25 mV above the individual open circuit potential for each sample to simulate minor oxidation. The individual potential was applied

Table 2
Galvanic couplings in synthetic sweat solution

Material coupling	Increased corrosion rate (mm/yr)
Ni-Sn + Brass (63% Cu, 37% Zn)	0.001
Ni-Sn + ASTM A284 steel	0.027
Ni-Sn + AISI 304	0.002
Ni-Sn + Zinc	1.047

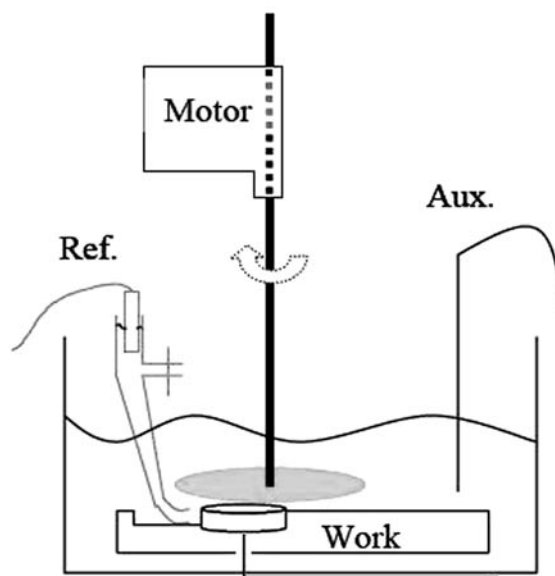


Figure 5—Tribocorrosion setup with motor, washable leather, auxiliary and reference electrode. The mounted sample acts as the working electrode.

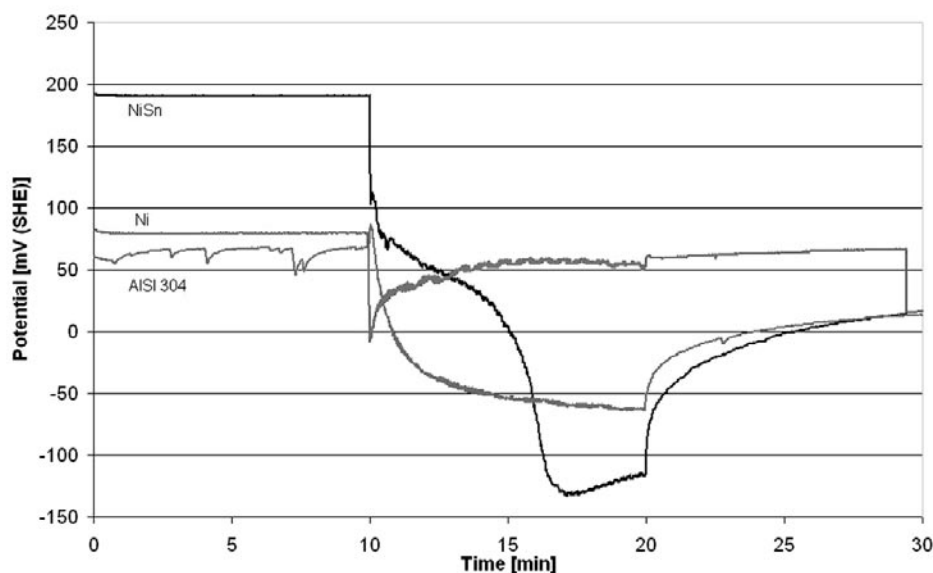


Figure 6—Open circuit potential measurements for NiSn, nickel and AISI 304 with and without the influence of wear. The open circuit potential was measured for 10 min and then the washable leather rotation was started. The rotation was stopped after 20 min.

at time zero. For NiSn, there was a rapid decrease in current after time zero due to passivation at this applied potential. After 10 min, there was a rapid increase in current density due to the start of the rotation of the washable leather. The increase in current was strongest in the case of NiSn at the applied potential 220 mV_{SHE}. As soon as the rotation stopped, the surface repassivated and the current decreased to a level similar to that before wear was introduced.

The increased corrosion rate observed under the wear test regime can explain the correlation discrepancy between *in-vivo* testing and electrochemical testing for Inconel® found earlier.¹⁰ The exposure to wear could have caused increased metal release and thereby nickel release. This could have caused the higher reactivity observed in the *in-vivo* test for Inconel.® It is also worth noticing that the European Standards EN 1811 and EN 12472 do not take the increased metal release during wear into account.

A comparison of the results indicates that NiSn was most susceptible to tribocorrosion at a constant potential of 220 mV_{SHE} when compared to austenitic stainless steel at 100 mV_{SHE} and nickel at 95 mV_{SHE}. Austenitic stainless steel seemed to be more susceptible to tribocorrosion than nickel. These findings are in accordance with the assumption that passive materials are more susceptible to altering corrosion behavior when exposed to wear, because of the destruction of the protective properties of the passive film.

Thermodynamic considerations

It is known that the NiSn alloy has properties that are not the average properties of nickel and tin separately, such as hardness and tarnish resistance. Table 3 shows that there was also a considerable change in the half-reaction standard potential when alloying the two elements.

The Pourbaix diagram shown in Fig. 8 is derived for a pressure of 1 bar (100 kPa; 14.5 lb/in²) and a temperature of 25°C (77°F). The diagram is derived for selected concentrations of ionic species (10⁻⁶M for nickel ions as well as tin, and 0.05M for chloride ions). Since X-ray investigations showed Ni₃Sn₂ to be dominant, Ni₃Sn₄, Ni₃Sn and nickel hydrides have been excluded from calculations, resulting in the diagram shown in Fig. 8.

The Pourbaix diagram shows stannic oxide (SnO₂) to be thermodynamically the most stable oxide. This does not necessarily mean that the oxide is of a protective (passivating) nature. Some kind

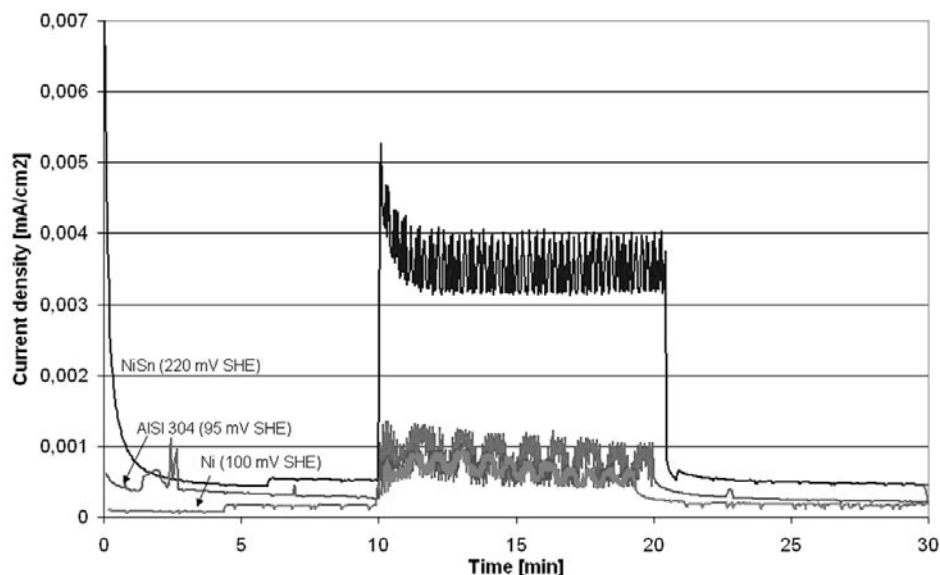


Figure 7—Chronoamperometric studies of nickel, AISI 304 and NiSn at a constant potential 25 mV above the corresponding individual open circuit potential.

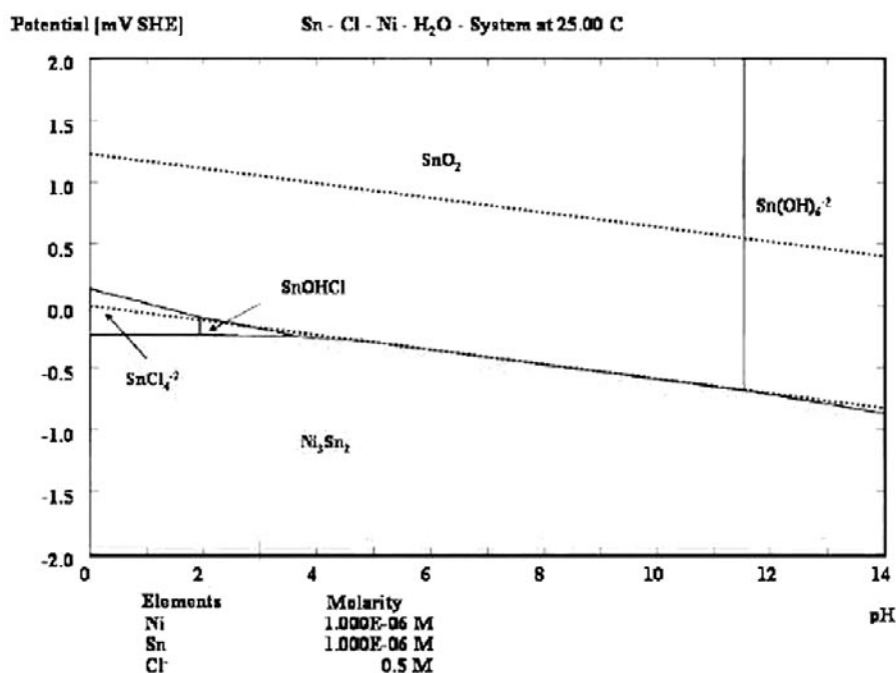


Figure 8—Simplified Pourbaix diagram for the Sn-Cl-Ni-H₂O system at 25°C (77°F).

Table 3
Half-reaction standard potentials at 20°C (68°F)

Reaction	E _{SHE} (mV)
Ni ⁺² + 2e ⁻ → Ni	-238
Sn ⁺² + 2e ⁻ → Sn	-141
3 Ni ⁺² + 2 Sn ⁺² + 10e ⁻ → Ni ₃ Sn ₂	-42

of passivating film is present on NiSn, accounting for its stability when exposed to concentrated nitric acid. At low pH values, Ni_3Sn_2 can transform into soluble tetrachlorostannate(II)⁻² ions (SnCl_4^{2-}) or tin(II) chloride hydroxide (Sn(OH)Cl). At high pH values, tin(IV) hexahydroxide⁻² ion (Sn(OH)_6^{2-}) is thermodynamically the most stable form. It should be emphasized that no information on corrosion kinetics is provided by this thermodynamically-derived diagram.

Conclusion

The structure of electrodeposited equiatomic NiSn alloy was determined by X-ray diffraction to consist mainly of Ni_3Sn_2 with a hexagonal structure of the NiAs type. The corrosion and tribocorrosion properties of the electrodeposited alloy were investigated in synthetic sweat solution by electrochemical techniques. The results show that NiSn had a passive behavior that exceeded that of stainless steel in synthetic sweat solution. Polarization curves also illustrated superior corrosion resistance for NiSn when compared to nickel. This was in accordance with earlier findings and is expected to be due to the passivity of NiSn alloys.

The passive film was studied earlier and was estimated to be approximately 30 Å thick, with a tin-rich oxide formed on the surface. Other investigations have shown that freshly fractured edges corrode severely compared to a passivated NiSn surface in the same environment. This work demonstrated that the corrosion properties of NiSn changed considerably when the deposit was exposed to wear, even to such a small degree as rubbing with washable leather. Our wear test apparatus was set up to simulate wear from handling with human fingers. Prior work has shown that the NiSn alloy did not release remarkable amounts of nickel when exposed to synthetic sweat solution, but further investigations must be made to evaluate how the deposit behaves when exposed to tribocorrosion.

The risk of increased metal release as a consequence of tribocorrosion can explain previous findings concerning discrepancies in electrochemical testing and *in-vivo* testing. This possible increased metal release is not taken into account in present European Standards evaluating nickel release.

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Jellesen



Møller

About the Authors

Morten S. Jellesen is currently studying for a Ph.D. degree at the Department of Manufacturing Engineering and Management, at the Technical University of Denmark (DTU), Lyngby. He holds a M.Sc. degree in chemical engineering from DTU.

Professor Per Møller received his Ph.D. in electroplating from Technical University of Denmark (DTU) in 1982. He has been Head of the Center of Advanced Electroplating, which was a part of The Danish Material Development Program with participation by several industrial companies. He has been a participant in a large number of surface technology projects in the European Union. Several of them have had a close relationship to research and education. Dr. Møller is currently employed at DTU as Professor in Corrosion and Surface Technology at the Technical University of Denmark. He has been a member of the AESF Research Board for many years.